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PROVISIONAL

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ORGANIC CHEMISTRY DIVISION
COMMISSION ON PHYSICAL ORGANIC CHEMISTRY*

GLOSSARY OF TERMS USED IN PHYSICAL ORGANIC CHEMISTRY

Compiled and Edited by
VICTOR GOLD

Comments on these proposals should be sent within 8 months of Publication to the Secretary of the Commission:

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Comments from the viewpoint of languages other than English are encouraged. These may have special significance regarding the eventual publication in various countries of translations of the nomenclature finally approved by IUPAC.

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GLOSSARY OF TERMS USED IN PHYSICAL ORGANIC CHEMISTRY

INTRODUCTION

At its first set of meetings, in September 1976, the recently constituted IUPAC Commission III.2 (Physical Organic Chemistry) initiated a project on the definition of terms used in Physical Organic Chemistry. It was noted that the formulation of novel scientific concepts was often arbitrary and unclear, and that scientific communication between physical organic chemists had been hampered by disagreement on the meaning of important terms. It was agreed that the progress of the subject could be helped by the compilation of a glossary of terms with the cooperation of active research workers, authors, and teachers of the subject.

With the help of an international group of ca. 30 original contributors a first draft of the glossary was compiled in May 1977 and was distributed to 120 chemists for comment. These comments were incorporated into a second draft (July 1977) which was considered at the second group of meetings of the Commission, in August 1977, when it was approved that I should refer some difficult and inconsistent sets of definitions to small authoritative working groups, again operating by correspondence. The expansion of some of the entries by the inclusion of clarifying examples was also recommended.

The resulting third draft, completed in March 1978, was sent for comment to ca. 150 chemists, including a high proportion of experts working in fields other than Physical Organic Chemistry. It was also distributed to the ca. 250 participants of the 4th International Conference on Physical Organic Chemistry in September 1978 and discussed during one of the plenary sessions. The Commission considered outstanding policy questions at its meeting during the same period. The responses received, both oral and written, together with provisional comments of IUPAC Commissions II.2 (Nomenclature of Inorganic Chemistry) and III.3 (Organic Photochemistry), and individual comments of members of Commission III.1 (Nomenclature of Organic Chemistry) and of the Sub-Committee on Nomenclature and Symbolism in Chemical Kinetics of Commission I.1 (Physicochemical Symbols, Terminology, and Units) were fully taken into account in the preparation of the final draft.

The names of the many people who have so generously helped, either by the formulation of draft definitions or by constructive criticism, are listed on a following page. However, inclusion in this list should not be taken as an individual's endorsement of the glossary or responsibility for its remaining flaws. Apologies are offered in advance for any inadvertent omission of the names of contributors.

The following criteria were adopted for the inclusion of a term, but it is inevitable that their application may be found to be somewhat subjective:

1. A term must be in current use by several independent authors or have been in such use until recently.

2. There must be some ambiguity or uncertainty in its usage by physical organic chemists or fairly widespread ignorance of its meaning. Alternatively, its specialist usage in Physical Organic Chemistry must significantly differ from the generally accepted definitions given in non-scientific dictionaries, or in standard chemistry text-books, or be inadequately dealt with in terminology reports of other IUPAC commissions. The most relevant of these reports are cited in the bibliography at the end of the glossary; their contents are intended to be complemented (and not repeated) by the present glossary.

The aim of the glossary is to provide guidance on physical-organic chemical terminology with a view to achieving a far-reaching consensus on the definition of useful terms and the abandonment of unsatisfactory or redundant ones. The Commission is anxious to emphasize that it cannot (and would not wish to) impose rules or restrictions, which might hinder rather than help the precise formulation of new ideas. Where the proper definition of other concepts required it, we have, sparingly and with due hesitation, introduced a few new terms, in the hope that they will gain acceptance on their merit. Attention is accordingly drawn to the entries chemical species, molecular entity, chemical flux and primitive change.

As a matter of policy, named reactions (such as Diels-Alder) and symbolic representations of mechanisms (S_N1, etc.) have been excluded. These topics are currently under consideration by other working parties of the Commission.

Generally speaking, operational definitions were preferred to definitions couched in terms of theoretical models. We have tried to avoid taking sides on issues of scientific, as distinct from semantic, disagreement. Similarly, we hope not to have incorrectly attributed named equations. With this kind of danger in mind, we have only sparingly inserted references to individual authors, either to indicate the origin of a term or to direct attention to a helpful, more elaborate discussion of a concept. It was felt justifiable to exclude named equations and effects that, at the time of compilation of this edition of the Glossary, would not normally be found in the literature without a source reference.

A dagger (†) against the title of an entry implies that we recommend discontinuation of its use.

The arrangement of entries is simply alphabetical. Underlined words in the body of a definition, as well as those cited at the end, point to relevant cross-references; double underlining implies that the cross-reference is of special importance to the entry in which it occurs. The appearance of a term in quotation marks in the body of a definition indicates that no further information will be found under that heading. A list of symbols used in the Glossary (and not explicitly defined each time they occur) is provided.

With a progressively evolving subject it is, of course, impossible to produce a set of definitions of indefinitely lasting validity. The revision of this Glossary of terms is therefore expected to remain a continuing responsibility of the Commission.

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LIST OF GENERAL SYMBOLS

A	pre-exponential factor in Arrhenius equation (see energy of activation).
a	parameter in empirical expression for rate constant (see enthalpy of activation).
α	order of reaction with respect to reactant A (see order of reaction).
b	parameter in empirical expression for rate constant (see enthalpy of activation).
β	order of reaction with respect to reactant B (see order of reaction).
C_p	heat capacity (at constant pressure).
c	parameter in empirical expression for rate constant (see enthalpy of activation).
d	parameter in empirical expression for rate constant (see enthalpy of activation).
E_a	energy of activation (see energy of activation).
G	Gibbs energy.
H	enthalpy.
h	Planck constant.
K	equilibrium constant.
k	rate constant (see order of reaction).
$\underline{k}$	Boltzmann constant.
λ	wavelength (of light).
ν	frequency (of light).
p	pressure.
R	gas constant.
S	entropy.
T	temperature.
t	time.
v	rate of reaction (see rate of reaction).
$\ddagger$	(superscript) relating to transition state).

GLOSSARY OF TERMS USED IN PHYSICAL ORGANIC CHEMISTRY

Abstraction reaction

A chemical reaction, the main feature of which is the bimolecular removal of an atom (neutral or charged) from a molecular entity. For example,

$$CH_3COCH_3 + CH_3CO_2^- \longrightarrow (CH_2COCH_3)^- + CH_3CO_2H$$

(proton abstraction from acetone)

$$CH_4 + Cl\cdot \longrightarrow \dot{C}H_3 + HCl$$

(hydrogen abstraction from methane)

Acid

See Brønsted acid, Lewis acid, hard acid, soft acid.

Acidity

(1) Of a compound:

The use of the term is usually restricted to Brønsted acids when it means the tendency of the compound to act as a proton donor. It can be quantitatively expressed by the acid dissociation constant of the compound in water or in some other specified medium. For Lewis acids it relates to the dissociation constants of Lewis adducts.

(2) Of a medium:

The use of the term is mainly restricted to Brønsted acids, when it means the tendency of the medium to protonate a specified reference base. It is quantitatively expressed by the appropriate acidity function.

Acidity function

Any quantitative scale that measures the thermodynamic proton-donating or -accepting ability of a solvent system or a closely related thermodynamic property, such as the tendency of the lyate ion of the solvent system to form Lewis adducts. (The term "basicity function" is not in common use in connection with basic solutions.) Commonly used acidity functions refer to concentrated acidic or basic solutions. They are evaluated by comparison of the protonation (or Lewis adduct formation) for a series of structurally similar indicator bases or acids of different strengths. The best known of these functions is the Hammett acidity function H_0 (for uncharged indicator bases that are aniline derivatives). For detailed information on other acidity functions, on the evaluation of acidity functions, and on the limitations of the concept, see ROCHESTER (1970).

Activated complex

This term is synonymous with transition state. Because of its more widespread usage the term transition state is preferred.

Activation energy

See energy of activation.

Addition

(1) Formation of an adduct.

(2) Loosely, an addition reaction.

Addition reaction

In organic chemistry, an (elementary or stepwise) reaction of the general type

$$XY + AB \longrightarrow XABY$$

involving a net reduction of bond multiplicity in AB. The multiple bond (or bonds) in AB may be contained within a cyclic structure.

The simplest types of addition reactions ("1,2-addition reactions") are those in which X and Y become linked to adjacent atoms, as in

$$Br_2 + CH_2{=}CH_2 \longrightarrow BrCH_2\text{-}CH_2Br$$

In other addition reactions X and Y become attached to non-adjacent atoms, as in the 1,4-addition reaction

$$Br_2 + CH_2{=}CH\text{-}CH{=}CH_2 \longrightarrow BrCH_2\text{-}CH{=}CH\text{-}CH_2Br$$

See also addition, cheletropic, cycloaddition.

Additivity principle

The hypothesis that each of several structural features of a molecular entity makes a separate and additive contribution to a property of the substance concerned. More specifically, it is the hypothesis that each of several substituent groups in a parent molecule makes a separate and additive contribution to the standard Gibbs energy change (or Gibbs energy of activation) corresponding to a particular equilibrium (or reaction rate). For further information and examples see BENSON (1976).

Adduct

A new chemical species AB formed by direct combination of two separate chemical species A and B in such a way that there is no change in connectivity of atoms within the moieties A and B. Stoichiometries other than 1:1 are also possible. An "intramolecular adduct" can be formed when A and B are groups contained within the same molecular entity.

This is a general term which, whenever appropriate, should be used in preference to the less explicit term complex. Examples are Lewis adduct, Meisenheimer adduct, π-adduct.

A-factor

See energy of activation.

Alcoholysis

See solvolysis.

α-Effect (*alpha*-Effect)

The enhancement of nucleophilicity that is found when the atom adjacent to a nucleophilic site bears a lone pair of electrons. For example, HO_2^- is more nucleophilic than HO^-.

α-Elimination (*alpha*-Elimination)

A reaction of the general type

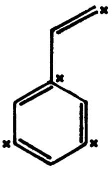
+ XY (or X + Y, or $X^+ + Y^-$)

where the central atom Z is most commonly carbon.

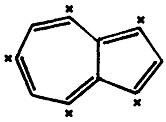
Alternant

A conjugated system is termed alternant if its atoms can be divided into two sets such that no atom of one set is directly linked to any other atom of the same set.

Example of alternant system:



Example of non-alternant system:

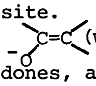


(Two atoms of the unstarred set are directly linked)

Alternant hydrocarbon

An alternant conjugated hydrocarbon, such as 1,3-butadiene, naphthalene, the allyl radical, and the benzyl radical.

Ambident

A description applied to a chemical species that possesses two alternative and strongly interacting distinguishable reactive centres to either of which a bond may be made in a reaction; the centres must be connected in such a way that reaction at either site stops or greatly retards subsequent attack at the second site. The term is most commonly applied to conjugated nucleophiles, such as the enolate ion  (which may react with electrophiles either at the β carbon atom or at oxygen) or γ-pyridones, and also to the vicinally ambident cyanide ion, nitrite ion, and unsymmetrical hydrazines.

Chemical species containing two non-interacting (or feebly interacting) reactive centres, such as the dianions of dicarboxylic acids, are not generally considered to be ambident and are better described as "bifunctional".

The Latin root of the word implies *two* reactive centres, but the term has in the past also incorrectly been applied to chemical species with more than two reactive centres. For such species the existing term "polydent" (or "multident") is more appropriate.

GOMPPER (1964)

SMITH and DeWALL (1977).

Amphiprotic (solvent)

Both protogenic and protophilic; for example, H_2O and CH_3OH.

Anchimeric assistance

See neighbouring-group participation.

Anionotropic rearrangement (or anionotropy)

See tautomerism.

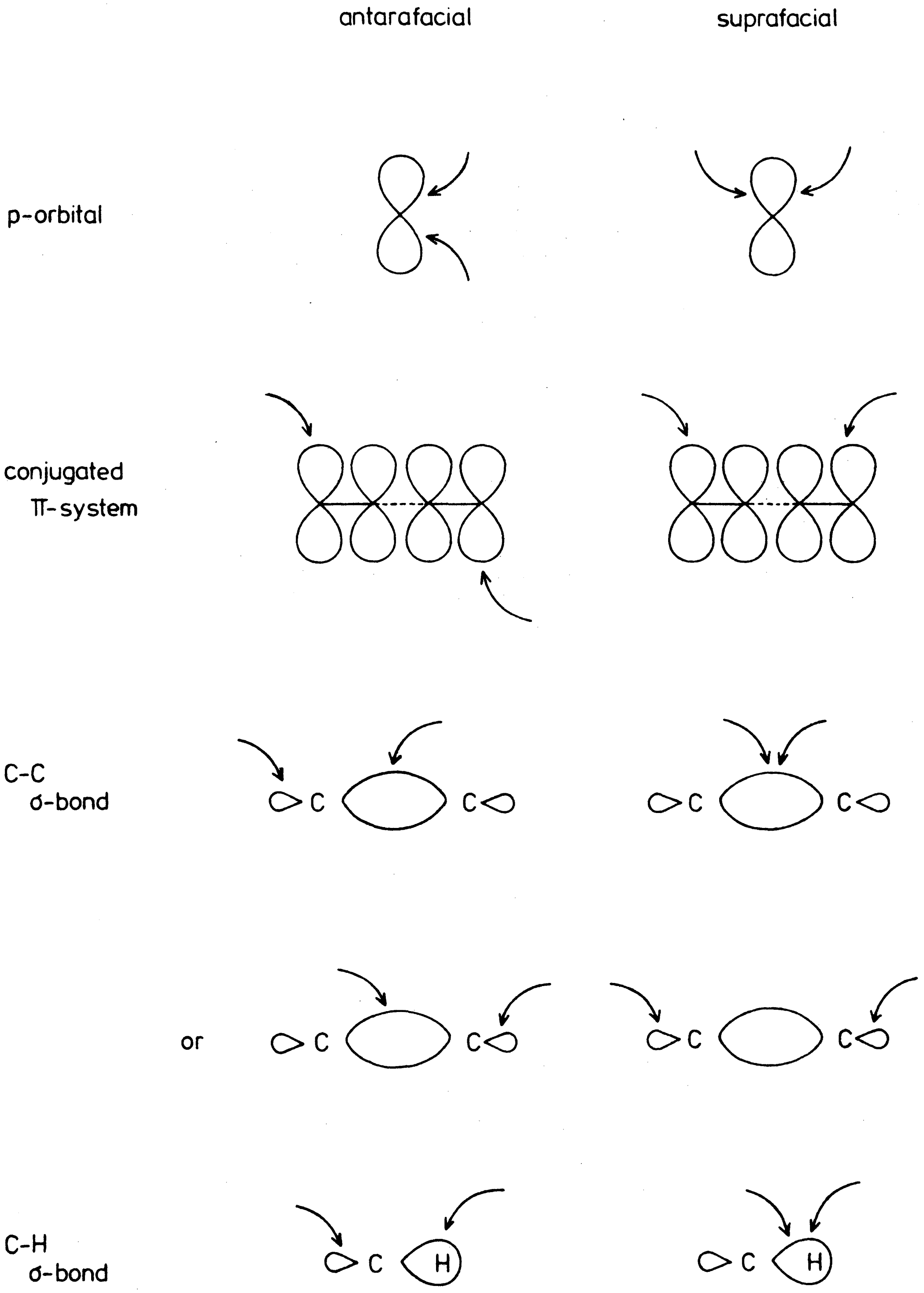
Anion radical

See radical anion.

Antarafacial and suprafacial

When a part of a molecule ("molecular fragment") simultaneously undergoes two changes in bonding to a common centre, or to two separate centres, external to itself, these bonding changes may be related in one of two spatially distinct ways; these are designated "antarafacial" if opposite faces of the molecular fragment are involved, and "suprafacial" if both changes occur at the same face. The distinction is self-explanatory when a p-orbital or conjugated π-electron system is involved (see diagrams). However, where a σ-bond is involved, suprafacial interactions may sometimes occur in more than one way. Thus, for a C-C σ-bond, the two suprafacial interactions may either be at the bonding faces of the tetrahedral carbon centres (reaction proceeding with retention of configuration at both centres), or they may be at the rear (non-bonded) faces (inversion resulting at both centres). The corresponding antarafacial changes proceed with inversion at one centre and retention at the other.

(The concept of "face" as used here, is related to simple ideas of orbital symmetry.)


antarafacial
suprafacial
p-orbital
conjugated π-system
C-C σ-bond
C
C
C
C
or
C
C
C
C
C-H σ-bond
C
H
C
H

Antiaromatic

See aromatic.

Anti-Markovnikov addition

See Markovnikov rule.

Aprotic (solvent)

Neither protogenic nor protophilic (in a given situation). (With extremely strong Brønsted acids or bases, solvents that are normally aprotic may accept or lose a proton. For example, acetonitrile is in most instances an aprotic solvent, but it is protophilic in the presence of concentrated sulphuric acid and protogenic in the presence of potassium *tert*-butoxide. Similar considerations apply to benzene, trichloromethane, etc.)

Aquation

The incorporation of one or more integral molecules of water into another species with or without displacement of one or more other atoms or groups (cf. hydration). For example, the substitution of water into the inner ligand sphere of an inorganic complex is an aquation reaction.

Aromatic

(1) In the traditional sense, "having a chemistry typified by benzene".

(2) A cyclically conjugated molecular entity with a stability (due to delocalization) significantly greater than that of a hypothetical classical structure (e.g., a Kekulé structure) [containing normal single and multiple bonds in fixed positions, and in which interactions between multiple bonds are assumed to be absent] is said to possess aromatic character. If the actual structure is of higher energy (less stable) than such a hypothetical classical structure, the molecular entity is "antiaromatic".

See also Hückel ($4n + 2$) rule, Möbius aromaticity. See ATKINS (1974).

(3) The terms aromatic and antiaromatic have been extended to describe the stabilization or destabilization of transition states of pericyclic reactions. The hypothetical reference structure is here less clearly identified, and use of the terms is based on application of the Hückel ($4n + 2$) rule and on consideration of the topology of orbital overlap in the transition state. Reactions involving antiaromatic transition states proceed much less easily (if at all) than those involving aromatic transition states.

DEWAR (1971)

ZIMMERMAN (1971).

Arrhenius energy of activation

See energy of activation.

Arrhenius equation

See energy of activation.

Association

The reverse of dissociation.

Asymmetric induction

The formation of a reaction product with a new chiral centre (and containing unequal amounts of the consequently generated stereoisomeric forms of the product) from a single precursor in which that centre was prochiral. Such a step requires the use of an optically active material (reagent, solvent, catalyst, enzyme, etc.) or an optically active precursor (in which case the chiral forms that are produced in unequal amounts are diastereoisomers).

Asymmetric induction in combination with separation processes may constitute an "asymmetric synthesis".

For the definition of the terms "chiral, "diastereoisomer","enantiomer", "prochiral", "stereoisomeric" see IUPAC ORGANIC STEREOCHEMISTRY RULES (1974).

Autocatalytic reaction

A chemical reaction in which a product (or a reaction intermediate) functions as a catalyst. In such a reaction the rate of reaction increases with time from its initial value.

Autoprotolysis

A proton transfer reaction between two identical molecules (usually of a solvent), one acting as a Brønsted acid and the other as a Brønsted base. For example:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Autoprotolysis constant

The product of the activities (or, more loosely, concentrations) of the species produced as the result of autoprotolysis. For solvents in which no other ionization processes are significant the term is synonymous with "ionic product" or "self-dissociation constant". The autoprotolysis constant for water K_w, is equal to the product of activities (H_3O^+) (OH^-) (1.0×10^{-14} mol^2 dm^{-6} at 25°C).

† Auxochrome

See chromophore.

† Azacarbene

See nitrene.

† Azene

See nitrene.

† Azylene

See nitrene.

Base

See Brønsted base, hard base, Lewis base, soft base.

Basicity function

See acidity function.

Bathochromic

The term refers to any effect on a chemical species (by a substituent, solvent, etc.) that causes its electronic absorption spectrum to be shifted to longer wave-lengths. The associated spectral shift is often referred to as a "bathochromic shift" or, somewhat misleadingly, as a "red-shift".

The opposite effect is called "hypsochromic" and the corresponding spectral shift to shorter wave-lengths ("hypsochromic shift") is, again somewhat misleadingly, widely known as a "blue-shift".

Bimolecular

Having a molecularity of two. The term describes an elementary reaction step having a transition state composed of the atoms of two initially separate molecular entities. For example: $Br^- + CH_3I \longrightarrow I^- + CH_3Br$.) For reactions in solution the solvent is considered as contributing to the molecularity only if it is covalently incorporated, wholly or partly, in the products of this step.

When applied to a reaction mechanism, the term signifies that the rate-limiting step is bimolecular.

See also unimolecular.

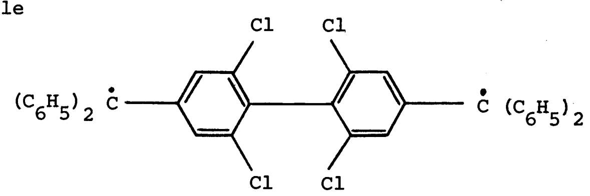
Binding site

A specific region (or atom) in a molecular entity that is capable of entering into a stabilizing interaction with another molecular entity. An example of such interaction is that of an active site in an enzyme with its substrate. Typical forms of interaction are by hydrogen bonding, co-ordination, and ion-pair formation.

Two binding sites in different molecular entities are said to be complementary if their interaction is stabilizing.

Biradical

A molecular entity in an electronic state described by a formula or by a combination of contributing structures containing two unpaired electrons in atomic orbitals on different atoms. For example



This term seems to be in more general use than the synonym "diradical", and is accordingly preferable.

See also carbene.

Bodenstein approximation

See steady state.

Bond (covalent bond)

A region of high electron density between atoms which arises at least partly from sharing of electrons and gives rise to an attractive force and characteristic internuclear distance between the atoms. For example: the C-H bond in hydrocarbons. The term "bond" should be avoided in describing attractive interactions between ions in crystals, van der Waals forces, and hydrophobic interactions.

See also co-ordination, dipolar bond, hydrogen bond, multi-centre bond.

Bond dissociation

See heterolysis, homolysis.

(In ordinary usage the term refers to homolysis only.)

Bond dissociation energy, D.

The enthalpy (per mole) required to break a given bond of some specific chemical species by homolysis, e.g., for $CH_4 \longrightarrow \cdot CH_3 + H\cdot$, symbolized as $D(CH_3\text{-}H)$; (cf. heterolytic bond dissociation energy.)

See also bond energy.

Bond energy (mean bond energy)

The average value of the gas-phase bond dissociation energies (usually at a temperature of 298K) of a given type of bond in the same chemical species. The mean C-H bond energy for methane, for example, is one-fourth the enthalpy of reaction for $CH_4(g) \longrightarrow C(g) + 4H(g)$.

Tabulated bond energies are generally values of mean bond energies averaged over a number of selected typical molecules containing that type of bond.

Bond migration

See migration.

Bond number

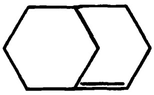
The number of electron-pair bonds between two nuclei in any given Lewis formula. For example, the bond number between the carbon atoms in ethylene (ethene) is two and between the carbon and hydrogen atoms it is one.

Bond order

A theoretical index of the degree of bonding between two atoms relative to that for a normal single bond, i.e., the bond provided by one localized electron pair. (In the valence-bond theory it is a weighted average of the bond numbers between the respective atoms in the contributing structures. In molecular-orbital theory it is calculated from the weights of the atomic orbitals in each of the occupied molecular orbitals.) For example, in valence-bond theory the bond order between adjacent carbon atoms in benzene is 1.5; in molecular-orbital theory it is 1.67.

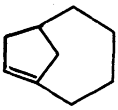
Bredt's rule

A double bond cannot be placed with one terminus at the bridgehead of a bridged ring system unless the rings are large enough to accommodate the double bond without excessive strain. This qualitative rule, originally formulated by J. Bredt, has been quantified by the proposal that the sum of the numbers of atoms (S-number) in the three bridges between the two bridgeheads of a bicyclic system determines whether that system can accommodate a bridgehead double bond. Compounds with $S \geqslant 7$ with a double bond at the bridgehead of a bicyclic system have been isolated: e.g.



Bicyclo[3.3.1]-non-1-ene

(S=7)



Bicyclo[4.2.1]-non-1(8)-ene

(S=7)

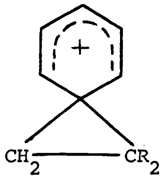
BREDT, THOUET and SCHMITZ (1924)

FAWCETT (1950)

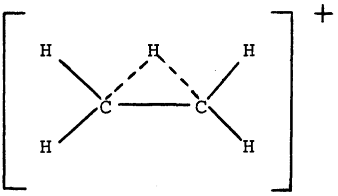
WISEMAN (1967).

Bridged carbocation

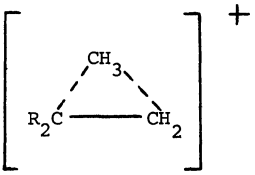
A carbocation (real or hypothetical) in which there are two (or more) carbom atoms that could in alternative Lewis formulae be designated as carbenium centres but which is instead represented by a structure in which a group (a hydrogen atom or a hydrocarbon residue, possibly with substituents in non-involved positions) bridges these potential carbenium centres. The bridging group thereby delocalizes the cationic charge. One may distinguish "electron-sufficient bridged carbocations" and "electron-deficient bridged carbocations". Examples of the former are phenyl-bridged ions (for which the trivial name "phenonium ion" has been used), such as (A). These ions are straightforwardly classified as carbenium ions. The latter type of ions necessarily involves three-centre bonding. Structures (C) and (D) contain penta-co-ordinate carbon atoms and are therefore classifiable as carbonium ions. The



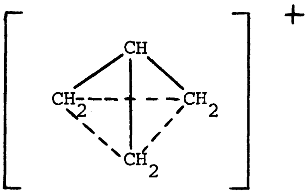
(A)



(B)



(C)



(D)

"hydrogen-bridged carbocation" (B) contains a di-co-ordinate hydrogen atom. (The above formulae are intended for purposes of definition only. Their inclusion has no bearing on the question whether or not they correspond to real chemical species.)

See also multi-centre bonding, neighbouring-group participation.

*Brønsted acid

A chemical species capable of donating a proton to a base, i.e. a "proton donor". For example: H_2O, H_3O^+, CH_3COOH, H_2SO_4, HSO_4^-.

*Brønsted base

A chemical species capable of accepting a proton from an acid i.e. a "proton acceptor". For example: OH^-, H_2O, CH_3COO^-, HSO_4^-, SO_4^{2-}.

*Brønsted catalysis law

See Brønsted relation.

*Brønsted exponent

See Brønsted relation.

*Brønsted relation

The name applies to either of the equations

$$k_{HA}/p = G(K_{HA}\,q/p)^{\alpha}$$

and $$k_A/q = G(K_{HA}\,q/p)^{-\beta}$$

where α, β and G are constant for a given reaction, (α and β are called Brønsted exponents), k_{HA} and k_A are catalytic constants (or rate constants of other reactions whose rates depend on the concentrations of HA and/or of A^-), K_{HA} is the acid dissociation constant of the acid HA, p is the number of equivalent acidic protons in the acid HA, and q is the number of equivalent basic sites in its conjugate base A^-. The chosen values of p and q should always be specified. (The charge designations on HA and A^- are only illustrative.)

The Brønsted relation is often termed the "Brønsted catalysis law" (or the "Catalysis law"). Although justifiable on historical grounds, this name is not recommended, since Brønsted relations are now known to apply to many uncatalysed reactions (such as simple proton transfer reactions).

See also linear Gibbs energy relation.

Cage

An aggregate of molecules, generally in the condensed phase, that surrounds the fragments formed by thermal or photochemical dissociation of a precursor species. Because the cage hinders the separation of the fragments by diffusion they may preferentially react with one another ("cage effect") but not necessarily to re-form the precursor species. For example,

$$\text{R-N=N-R} \xrightarrow[\Delta]{} \underset{cage}{[\text{R}\cdot + \text{N}\equiv\text{N} + \text{R}\cdot]} \longrightarrow \text{R-R} + \text{N}_2$$

See also geminate recombination.

Cage compound

(1) See clathrate.

(2) A compound possessing a non-planar bi- or poly-cyclic molecular structure enclosing a cavity.

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* The spelling "Brønsted" may be transliterated as "Brönsted".

Canonical form

See contributing structure.

Carbanion

An anion containing an even number of electrons in which a significant portion of the excess negative charge is located on one or more carbon atoms. For example: H_3C^-, the methyl anion.

Carbene

The species $\ddot{C}H_2$ or a substitution derivative thereof, containing neutral divalent carbon with two nonbonding electrons. The nonbonding electrons may have antiparallel spins (singlet state) or parallel spins (triplet state).

(As a generic term the name is preferred to the alternative "methylene".)

See also biradical.

Carbenium centre

The carbon atom in a carbenium ion on which the excess positive charge of the ion (other than that located on heteroatoms) may be considered to be largely concentrated. (N.B.: It is not always possible to identify such an atom.)

Carbenium ion

A carbocation, real or hypothetical, that contains at least one trivalent carbon atom in one of its important contributing structures. (The name implies a protonated carbene or a substitution derivative thereof.)

The term is intended to replace the *older* usage of the name carbonium ion.

To avoid ambiguity, the name should not be used as the root for the systematic nomenclature of carbocations. Such ions should be named by adding the word "cation" to the name of the corresponding radical [IUPAC ORGANIC RULES (1969), Rule C-83.1, alternative (*a*)]. The corresponding ambiguity has confused carbonium ion nomenclature for many years. For example, the term "ethyl carbonium ion" has at times been used to refer either to $CH_3CH_2^+$ or to $CH_3CH_2CH_2^+$.)

Carbocation

A cation containing an even number of electrons in which a significant portion of the excess positive charge is located on one or more carbon atoms.

See also bridged carbocation, carbenium ion, carbonium ion.

Carbonium ion

A carbocation, real or hypothetical, that contains at least one penta-co-ordinate carbon atom. The term should be used with great care since it is also the traditional name for what is here defined as carbenium ion. In most of the existing literature the term is used in that sense. [See also IUPAC ORGANIC RULES (1969), Rule C-83.1].

To avoid ambiguity the name should never be used as the root for the systematic nomenclature of carbocations.

Carbyne

The electrically neutral species $\cdot\ddot{C}H$ or a substitution derivative thereof, (such as $\cdot\ddot{C}$-CO_2Et). Use of the alternative name "methylidyne" as a generic term is not recommended.

Carbynium ion

There is confusion concerning the meaning of this term, which has been used in two senses.

1. The cationic species $\cdot CH_2^+$ (protonated carbyne) or a substitution derivative thereof.

†2. A vinyl cation.

It is recommended that the use be restricted to (1).

Catalysis

The action of a catalyst.

Catalysis law

See Brønsted relation.

Catalyst

A substance that participates in a particular reaction and thereby increases its rate but without being destroyed by that reaction (or incorporated into the products). At the molecular level, the catalyst is regenerated after each transformation of reactant to product.

See also autocatalytic reaction, general acid catalysis, general base catalysis, intramolecular catalysis, promotion, specific catalysis.

Catalytic constant

If the rate of reaction (v) of a reaction is expressible in the form

$$v = \left(k_0 + \sum_i k_i [C_i]^{n_i}\right)[A]^\alpha [B]^\beta \ \ldots$$

where A, B, ... are reactants and C_i represents one of a set of i catalysts, then the proportionality factor k_i is the catalytic constant of the particular catalyst C_i. Normally the partial order of reaction n_i with respect to a catalyst will be unity, so that k_i is an $(\alpha + \beta + \ldots + 1)$th order rate constant. The proportionality factor k_0 is the $(\alpha + \beta + \ldots)$th order rate constant of the uncatalysed component of the total reaction.

Cationotropic rearrangement (cationotropy)

See tautomerism.

Cation radical

See radical cation.

Chain reaction

A reaction in which one or more reactive reaction intermediates (frequently radicals) are continuously regenerated, usually through a repetitive cycle of elementary steps (the "propagation steps"). For example, in the free radical chlorination of methane, Cl· is continuously regenerated in the chain propagation steps.

$$\left.\begin{array}{l} Cl\cdot + CH_4 \longrightarrow HCl + \cdot CH_3 \\ \cdot CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\cdot \end{array}\right. \qquad \text{Propagation steps}$$

In polymerization reactions, reactive intermediates of the same type, generated in successive steps or cycles of steps, differ in molecular mass, as in

$$R\dot{C}HCH_3 + CH_2{=}CHCH_3 \longrightarrow RCH(CH_3)CH_2\dot{C}HCH_3$$

See also chain transfer, initiation, termination.

Chain transfer

The abstraction, by the radical end of a growing chain-polymer, of an atom from another molecule. The growth of the polymer chain is thereby terminated but a new radical, capable of chain propagation and polymerization, is simultaneously created. For the example of olefin polymerization cited for a chain reaction, the reaction

$$R\dot{C}HCH_3 + CCl_4 \longrightarrow RCHClCH_3 + \dot{C}Cl_3$$

represents a chain transfer, the radical $\dot{C}Cl_3$ propagating further polymerization:

$$CH_2{=}CHPh + Cl_3\dot{C} \longrightarrow Cl_3CCH_2\dot{C}HPh$$

$$Cl_3CCH_2CHPh + CH_2{=}CHPh \rightarrow Cl_3CCH_2CHPhCH_2\dot{C}HPh \quad etc.$$

Charge density

The probability (per unit volume) of unit charge being in an infinitesimal volume element around a given point. It is equal to the electron density, multiplied by the magnitude (amplitude) of the electronic charge.

Charge population

The net electric charge on a specified atom in a molecule, as determined by some prescribed definition: it is not physically observable.

See also electron density.

Charge transfer complex

A complex whose nature is indirectly inferred mainly from optical absorption (or absorptions) corresponding to electronic transition(s) to an excited state in which there is a partial transfer of electronic charge from the electron donor to the electron acceptor moiety.

$$(D + A \rightleftharpoons DA \xrightarrow{h\nu} D^{\delta+} A^{\delta-})$$

The term need not be taken to imply that charge transfer is responsible for bonding in such complexes. Whilst complexes between molecules of high electron affinity and low ionization energy are frequently observed, there is disagreement concerning the cause of the attraction between the moieties.

Chelate

See chelation.

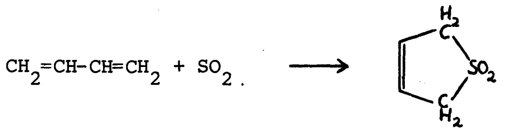
Chelation

Chelation is the formation or presence of bonds from two or more atoms within the same ligand to a single central atom. A chemical species in which there is chelation is called a "chelate". The terms bidenate, tridentate ... polydentate are used to indicate the number of binding sites. For example the bidentate ethylenediamine forms a chelate with Cu^{I} in which both nitrogen atoms of ethylenediamine are bonded to copper. (The use of the term is often restricted to metallic central atoms.)

See also cryptand, cryptate.

Cheletropic reactions

A "cheletropic addition" is a form of cycloaddition across the terminal atoms of a fully conjugated system with formation of two new σ-bonds to a single atom of the ("monocentric") reagent. There is a formal loss of one π-bond in the substrate and an increase in co-ordination number of the relevant atom of the reagent. An example is the addition of sulfur dioxide to butadiene:



The reverse of this type of reaction is designated "cheletropic elimination".

†Chelotropic reactions

Alternative name for cheletropic reactions.

Chemical flux

A concept related to rate of reaction, particularly applicable to the progress in one direction only of component reaction steps in a complex system or to the progress in one direction of reactions in a system at dynamic equilibrium (in which there are no observable concentration changes with time). Chemical flux (ϕ) is a derivative with respect to time, and has the dimensions of amount of substance per unit volume transformed per unit time.

The sum of all the chemical fluxes leading to destruction of B is designated the "total chemical flux out of B" (symbol $\Sigma\phi_{-B}$); the corresponding formation of B by concurrent elementary reactions is the "total chemical flux into B" (symbol $\Sigma\phi_{B}$)

For the mechanism

$$A + B \underset{-1}{\overset{1}{\rightleftharpoons}} C$$

$$C + D \xrightarrow{2} E$$

the total chemical flux into C is caused by the single reaction (1):

$$\Sigma\,\phi_{C} = \phi_{1}$$

whereas the chemical flux out of C is a sum over all reactions that remove C:

$$\Sigma\phi_{-C} = \phi_{-1} + \phi_{2}$$

where ϕ_{-1} is the "chemical flux out of C into B" and ϕ_{2} is the "chemical flux out of C into E".

The rate of appearance of C is then given by

$$\frac{d[C]}{dt} = \Sigma\phi_{C} - \Sigma\phi_{-C}$$

In this system ϕ_{1} (or $\Sigma\phi_{-A}$) can be regarded as the hypothetical rate of decrease in the concentration of A due to the single (uni-directional) reaction (1) proceeding in the assumed absence of all other reactions.

For an *irreversible reaction* $A \xrightarrow{1} P$,

$$-\frac{d[A]}{dt} = \phi_{1}$$

If two substances A and P are in *chemical equilibrium*($A \rightleftharpoons P$), then

$$\Sigma\phi_{A} = \Sigma\phi_{-A} = \Sigma\phi_{P} = \Sigma\phi_{-P}$$

and

$$-\frac{d[A]}{dt} = \frac{d[P]}{dt} = 0$$

See also, order of reaction, rate-limiting step, steady state.

Chemical reaction

Any single process or operation involving the interconversion of chemical species. It may be composed of several elementary reactions. (It should be noted that this definition includes the interconversion of separately distinguishable conformers.)

Chemical species

A set of chemically identical molecular entities, the members of which have the same composition and can explore the same set of molecular energy levels on the time scale of the experiment.

For example, two conformational isomers may interconvert sufficiently slowly to be detectable by separate NMR spectra and hence to be considered to be separate chemical species on a time scale governed by the radiofrequency of the spectrometer used. On the other hand, in a slow chemical reaction the mixture of conformers may behave as a single chemical species, i.e. there is virtually complete equilibrium population of the set of molecular energy levels.

Except where the context requires otherwise, the term is taken to refer to a set containing molecular entities having the natural abundance of isotopes.

In common chemical usage, and in this Glossary, generic and specific chemical names (such as radical or hydroxide ion) refer to either a chemical species or to a molecular entity.

Chemically induced dynamic nuclear polarization

See CIDNP.

Chemoselective, chemoselectivity

Chemoselectivity is the preferential reaction of a chemical reagent with one of two or more different functional groups. A reagent has a high chemoselectivity if reaction occurs with only a limited number of different functional groups. For example, sodium borohydride is a more chemoselective reducing agent than is lithium aluminium hydride.

The concept has not been defined in more quantitative terms.

Chromophore

One of the groupings within a molecular entity to which the colour of a substance is attributed, or, in modern terms, the region in a molecular entity in which the associated electronic transition is thought to be more or less localized. The more restricted concept arose out of the empiricism of dyestuff chemistry. A grouping which, though not capable of conferring colour on a substance by itself, is capable of "augmenting" the action of a chromophore (and thereby of modifying the colour) was called an "auxochrome" (a term not in current use).

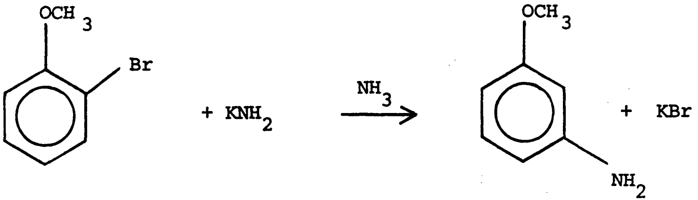
WITT (1876).

CIDNP (Chemically induced dynamic nuclear polarization)

An effect sometimes encountered in the NMR spectra of products of reactions that proceed by way of free radical intermediates, when these spectra are recorded while the reaction is taking place or immediately thereafter. The effect is manifest in the form of a distortion of the intensity of NMR absorption signals, the appearance of signals in emission, or abnormal intensity ratios in spin multiplets. These transient spectral abnormalities result from a non-Boltzmann distribution of nuclear spin populations, attributed to spin correlation effects within radical pairs which are the precursors of the observed products. Since the spin populations of the products rapidly attain a normal Boltzmann distribution, the effect decays rapidly after reaction is complete.

Cine-substitution

A substitution reaction (generally aromatic) in which the entering group takes up a position adjacent to that occupied by the leaving group. For example,



See also tele-substitution.

Class (a) metal ion

A metal ion that combines preferentially with ligands containing ligating atoms that are the lightest of their Periodic Group.

See also class (b) metal ion, hard acid, soft acid.

Class (b) metal ion

A metal ion that combines preferentially with ligands containing ligating atoms other than the lightest of their Periodic Group.

See also class (a) metal ion, hard acid, soft acid.

Clathrate

The same as inclusion compound, except that the spaces in the crystal lattice that contain the guest molecules are completely enclosed. Clathrates are also known as "cage compounds".

See also guest, host molecule.

Colligation

The formation of a covalent bond by the combination or recombination of two radicals (the reverse of unimolecular homolysis). For example: $CH_3\cdot + OH\cdot \rightarrow CH_3OH$

See also dimerization.

Common-ion effect (on rates)

A reduction in the rate of a chemical reaction of a substrate RX in solution [by a path that involves a pre-equilibrium with formation of R^+ (or R^-) ions as reaction intermediates], caused by the addition to the reaction mixture of an electrolyte solute containing the "common ion" X^- (or X^+). For example, the rate of solvolysis of diphenylmethyl chloride in acetone-water is reduced by the addition of salts of the common ion Cl^- which causes a decrease in the quasi-equilibrium concentration of the diphenylmethyl cation in the scheme

$$RCl \underset{-1}{\overset{1}{\rightleftharpoons}} R^+ + Cl^- \quad \text{(free ions, \textit{not} ion pairs)}$$

$$R^+ + OH_2 \xrightarrow{2} ROH + H^+ \quad \text{(solvated)}$$

provided $\phi_2 \not\gg \phi_{-1}$ (where ϕ = chemical flux).

This phenomenon is directly related to - and a consequence of - the familiar common-ion effect on ionization equilibria, commonly met in the context of electrolyte solubility, for example.

Complementary binding sites

See binding site.

Complex

A distinct chemical species formed by a loose association involving two or more chemical species (ionic or uncharged). The binding between the components is normally weaker than in a covalent bond.

The term has also been used with a variety of shades of meaning in different contexts: it is therefore best avoided when a more explicit alternative is applicable. For the different usage of "complex" in inorganic chemistry, see IUPAC INORGANIC RULES (1970); Rule 2.24.

See also, activated complex, adduct, charge transfer complex, electron-donor-acceptor complex, encounter complex, π-adduct.

Comproportionation

The reverse of disproportionation.

Concerted (process)

Two or more primitive changes are said to be concerted (or to constitute a concerted process) if they occur within the same elementary reaction step. Such changes will normally (though perhaps not inevitably) be "energetically coupled". (In the present context the term "energetically coupled" means that the simultaneous progress of the primitive changes is energetically more favourable than their successive occurrence.)

See also potential energy reaction surface, synchronous.

Condensation reaction

A (usually stepwise) reaction in which two or more reactants (or remote reacting sites within the same molecular entity) yield a single main product with accompanying formation of water or of some other small molecule, e.g., ammonia, ethanol, acetic acid, hydrogen sulfide.

The mechanism of many condensation reactions has been shown to comprise consecutive addition and elimination reactions, as in the base-catalysed formation of *trans*-but-2-enal (crotonaldehyde) from acetaldehyde, via 3-hydroxybutenal (aldol). The overall reaction is known as the aldol condensation.

$$2CH_3CHO \xrightarrow[\text{reaction}]{\text{Addition}} \underset{\text{aldol}}{CH_3CH(OH)CH_2CHO} \xrightarrow[\text{reaction}]{\text{Elimination}} CH_3CH{=}CHCHO + H_2O$$

Configuration

See IUPAC ORGANIC STEREOCHEMISTRY RULES (1974).

Conformation

See IUPAC ORGANIC STEREOCHEMISTRY RULES (1974).

Conjugate acid-base pair

The Brønsted acid BH^+ formed on protonation of a base B is called the conjugate acid of B, and B is the conjugate base of BH^+. (The conjugate acid always carries one unit positive charge more than the base, but the absolute charges of the species are immaterial to the definition.) For example: the Brønsted acid HCl and its conjugate base Cl^- constitute a conjugate acid-base pair.

Conjugated system

See conjugation.

Conjugation

An alternating sequence of single and multiple bonds containing at least two multiple bonds. The structural unit containing such a sequence is called a "conjugated system". In more recent usage the term has been applied to the overlap of atomic p orbitals of three or more adjacent atoms.

See also homoconjugation, resonance, delocalization.

Conjugation mechanism

See electromeric effect.

Connectivity

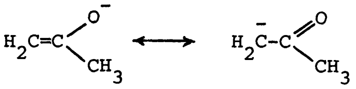
In a chemical context, the information content of a line formula, but omitting any indication of bond multiplicity.

Contact ion pair

See ion pair.

Contributing structure

The definition is based on the valence-bond formulation of the quantum-mechanical idea of the wave function of a molecule as composed of a linear combination of wave functions, each representative of a formula containing bonds that are only single, double, or triple with a particular pairing of electron spins. Each such formula represents a contributing structure to the total wave function, and the degree to which each contributes is indicated by the square of its coefficient in the linear combination. The contributing structures themselves thus have a purely formal significance: they are the components from which wave functions can be built. Structures may be covalent (or non-polar) or ionic (or polar). The representation is frequently kept rather qualitative so that we speak of important or major contributing structures and minor contributing structures. For example, two major non-equivalent contributing structures to the conjugate base of acetone are



See also Kekulé structure, resonance, delocalization.

†Co-ordinate covalence (co-ordinate link)

See co-ordination.

Co-ordination

A covalent bond the two shared electrons of which have come from only one of the two parts of the molecular entity linked by it, or the formation of such a bond, as in the reaction between a Lewis acid and a Lewis base to form a Lewis adduct. It is the reverse of unimolecular heterolysis.

(The origin of the bonding electrons has by itself no bearing on the character of the bond formed. Thus, the formation of methyl chloride from a methyl cation and a chloride ion involves co-ordination; the resultant bond obviously differs in no way from the C-Cl bond in methyl chloride formed by any other path, e.g., by colligation of a methyl radical and a chlorine atom.)

See also dipolar bond, π-adduct.

Co-ordination number

The co-ordination number of a specified atom in a chemical species is the number of other atoms directly linked to that specified atom [cf. IUPAC INORGANIC RULES (1970); Rule 0.2]. For example, the co-ordination number of carbon in methane is four. (The term is used in a different sense in the crystallographic description of ionic crystals.)

Cosphere

See cybotactic region.

Couper-Butlerow structure

See line formula.

Critical micelle concentration (CMC)

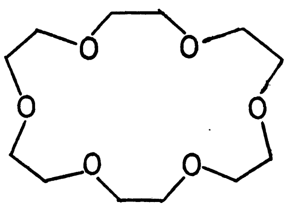
See IUPAC MANUAL APPENDIX II (1972).

See also inverted micelle.

Cryptand

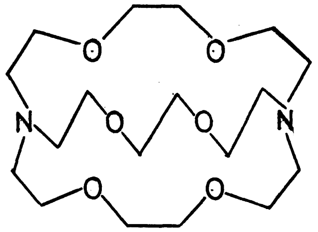
A molecular entity comprising a cyclic (monocyclic or polycyclic) ligand assembly that contains four or more binding sites held together by covalent bonds in such a way as to bind (and thus "hide" in a cavity) another molecular entity (typically a metal cation) more strongly than the separate parts of the assembly (at the same total concentration of binding sites) do. The adduct thus formed is called a "cryptate".

Examples include



("18-crown-6")

and



Coplanar cyclic polydentate ligands, such as porphyrins, are *not* normally regarded as cryptands.

Cryptate

See cryptand.

Curtin-Hammett principle

In a chemical reaction that yields one product from one conformational isomer and a different product from another conformational isomer (and provided these two isomers are rapidly interconvertible relative to the rate of product formation, whereas the products do not interconvert) the product composition does not depend on the relative proportions of the conformational isomers in the substrate but only on the standard Gibbs energies of the respective transition states.

See also chemical species.

Cybotactic region

That part of a solution in the vicinity of a solute molecule in which the ordering of the solvent molecules is modified by the presence of the solute molecule. The term solvent "cosphere" of the solute has also been used.

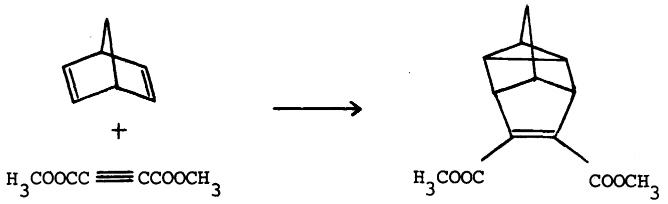
See also solvation.

Cycloaddition

A reaction in which two or more unsaturated molecules (or parts of the same molecule) combine with the formation of a cyclic product in which unsaturation has been reduced.

The following two systems of notation have been used for the more detailed specification of cycloadditions, of which the second, more recent system is preferred:

(1) An $[i+j]$ cycloaddition is a reaction in which two molecules (or parts of the same molecule) respectively provide units of i and j linearly connected atoms; and these units become joined at their respective termini by new σ-bonds so as to form a cycle containing $(i+j)$ atoms. In this notation, (a) a Diels-Alder reaction is a [2+4] cycloaddition, (b) the initial reaction of ozone with an alkene is a [2+3] cycloaddition, and (c) the reaction shown below is a [2+2+2] cycloaddition (where the system of notation is extended to the cycloaddition of three reactant units).



(2) An $[i+j]$ cycloaddition identifies the numbers (i and j) of electrons (further specified as subscript) in the interacting units that participate in the transformation of reactants to products. In this notation the reactions (a) and (b) of the preceding paragraph would both be described as $[{}_{\pi}2 + {}_{\pi}4]$ cycloadditions, and (c) as a $[{}_{\pi}2 + {}_{\pi}2 + {}_{\pi}2]$ cycloaddition.

Cycloadditions may be concerted (pericyclic) processes or (non-concerted) stepwise reactions.

See also cheletropic reactions.

Cycloelimination

See cycloreversion.

Cycloreversion

The reverse of cycloaddition. It is alternatively referred to as "cycloelimination", "retroaddition" or "retrocycloaddition".

†Dative bond

See co-ordination.

Decomposition (chemical)

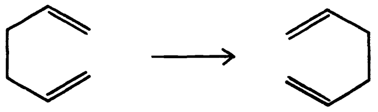
The breakdown of a single entity (normal molecule, reaction intermediate, etc.) into two or more fragments.

Degenerate chemical reaction

See identity reaction.

Degenerate rearrangement

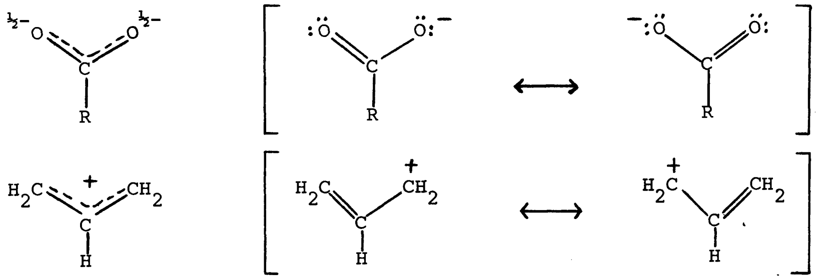
A molecular rearrangement in which the principal product is indistinguishable from the principal reactant. The term includes both "degenerate intramolecular rearrangements" and reactions that involve intermolecular transfer of atoms or groups ("degenerate intermolecular rearrangements"): both are degenerate isomerizations. The occurrence of degenerate rearrangements may be detectable by isotopic labelling or by dynamic NMR techniques. For example: the [3,3]sigmatropic rearrangement of 1,5-hexadiene,



See also fluxional, molecular rearrangement.

Delocalization

A quantum-mechanical concept directly associated with the Uncertainty Principle, most usually applied in organic chemistry to describe the π-bonding in a conjugated system. This bonding is not localized: instead, each link has a "fractional double bond character" or bond order. There is a corresponding "delocalization energy", identifiable with the stabilization of the system compared with a hypothetical alternative in which formal (localized) single and double bonds are present. Some degree of delocalization is always present, and can be estimated by quantum-mechanical calculations. The effects are particularly evident in aromatic systems and in symmetrical molecular entities in which a lone pair or a vacant p orbital is conjugated with a double bond (e.g. carboxylate ions, nitro compounds, the allyl cation). Delocalization in such species may be represented by partial bonds or as resonance (here symbolized by a two-headed arrow) between contributing structures, e.g.



These examples also illustrate the concomitant delocalization of charge in ionic conjugated systems. Analogously, delocalization of the spin of an unpaired electron occurs in conjugated radicals.

See also mesomerism.

Detailed balancing, Principle of

When equilibrium is reached in a reaction system (containing however many components and reaction paths) as many atoms, in their respective molecular entities, will pass forwards as backwards along each individual path in a given finite time interval. Accordingly, the mechanism of a reaction in the reverse direction must in every detail be the reverse of the mechanism in the forward direction (provided always that the system is at or near equilibrium): this need not be true when the system is far from equilibrium.

The principle of detailed balancing is a consequence for macroscopic systems of the principle of microscopic reversibility.

Diffusion-controlled rate

See encounter-controlled rate, macroscopic diffusion control, microscopic diffusion control.

Dimerization

The reaction of a chemical species A to give a chemical species A_2. For example:

$H_3C\cdot + \cdot CH_3 \longrightarrow CH_3CH_3$, or $2\ CH_3COCH_3 \longrightarrow (CH_3)_2\ C(OH)CH_2\ COCH_3$

†Dipolar-aprotic solvent

A solvent with a relatively high relative permittivity (or dielectric constant), greater than ca. 15, that cannot donate suitably labile hydrogen atoms to form strong hydrogen bonds, e.g., dimethyl sulfoxide. The term (and its alternative "polar-aprotic solvent") is a misnomer and should therefore be discouraged. Such solvents are not aprotic but may be protophilic and/or weakly protogenic. In describing a solvent is is better to be explicit about its essential properties, e.g., dipolar and non-hydroxylic.

Dipolar bond

A bond formed (actually or conceptually) by co-ordination of two neutral moieties, e.g.,

$$R_3N: \ + \ \ddot{\underset{\cdot\cdot}{O}}: \longrightarrow R_3\overset{+}{N}\text{-}O^-$$

The term is preferred to the obsolescent or obsolete synonyms "co-ordinate link", "co-ordinate covalence", "dative bond", "semipolar double bond".

†Diradical

See biradical

Direct effect

See field effect.

Disproportionation

Any reaction of the type $A + A \longrightarrow A' + A''$ where A,A' and A" are different chemical species. For example:

$$2ArH^{\bullet -} \longrightarrow ArH + ArH^{2-}$$

The reverse of disproportionation is called "comproportionation".

A special case of disproportionation is "radical disproportionation", exemplified by

$$\cdot CH_2CH_3 \ + \ \cdot CH_2CH_3 \longrightarrow CH_2{=}CH_2 \ + \ CH_3CH_3$$

Reactions of the more general type

$$RCHCH_3 \ + \ R'\dot{C}HCH_3 \longrightarrow RCH{=}CH_2 \ + \ R'CH_2CH_3$$

are also loosely described as radical disproportionations.

(A somewhat more restricted usage of the term prevails in inorganic chemistry.)

Dissociation

(1) The separation of a molecular entity into two or more molecular entities. Examples include unimolecular heterolysis and homolysis, and the separation of the constituents of an ion pair into free ions.

(2) The separation of the constituents of any aggregate of molecular entities.

Driving force

The difference in Gibbs energy between the products and reactants of a chemical reaction (ΔG).

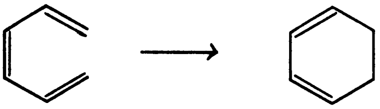
Effective molarity

The ratio of the first-order rate constant of an intramolecular reaction involving two functional groups within the same molecular entity to the second-order rate constant of an analogous intermolecular elementary reaction. This ratio has the dimensions of concentration.

See also intramolecular catalysis.

Electrocyclic

An electrocyclic reaction is a pericyclic intramolecular rearrangement that involves an increase by one in the number of σ-bonds and a decrease by one in the number of π-bonds, or vice versa. For example,



See also molecular rearrangement.

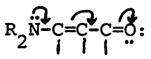
Electrofuge

A leaving group that does not carry away the bonding electron pair. The leaving tendency of such a group (an electrofugic group) has been called electrofugicity. (The occasionally encountered alternative, electrofugacity, is misleading and should not be used.)

See also electrophile, nucleofuge.

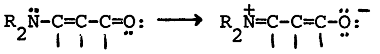
†Electromeric effect (obsolescent)

A molecular polarizability effect occurring by an intramolecular electron displacement (sometimes called the "conjugative mechanism" and, previously, the "tautomeric mechanism") characterized by the substitution of one electron pair for another within the same atomic octet of electrons. It can be indicated by curved arrows symbolizing the displacement of electron pairs, as in



$$R_2\ddot{N}-\underset{|}{C}=\underset{|}{C}-\underset{|}{C}=\underset{\cdot\cdot}{O}:$$

which represents the *hypothetical* conversion



$$R_2\ddot{N}-\underset{|}{C}=\underset{|}{C}-\underset{|}{C}=\underset{\cdot\cdot}{O}: \longrightarrow R_2\overset{+}{N}=\underset{|}{C}-\underset{|}{C}=\underset{|}{C}-\underset{\cdot\cdot}{\ddot{O}}:^{-}$$

See INGOLD (1953).

Electron acceptor

(1) A substance to which an electron may be transferred; for example, 1,4-dinitrobenzene or the 1,1'-dimethyl-4,4'-bipyridylium dication.

†(2) A Lewis acid. This usage is discouraged.

Electron affinity

The energy (enthalpy) released when an additional electron (without excess energy) attaches itself to a molecular entity (usually an electrically neutral molecular entity). (The direct measurement of this quantity involves molecular entities in the gas phase.)

Electron density

The electron probability distribution in a molecular entity. If $P(x,y,z)\,dx\,dy\,dz$ is the probability of finding an electron in the volume element $dx\,dy\,dz$ at the point with co-ordinates x,y,z then $P(x,y,z)$ is the electron density. For many purposes (e.g., x-ray scattering, forces on atoms) the system behaves exactly as if the electrons were smeared out into a continuously distributed charge. The term has frequently been wrongly applied to negative charge population.

See also charge density.

Electron donor

(1) A substance that can transfer an electron to another chemical species; for example, the naphthalene radical anion.

†(2) A Lewis base. This usage is discouraged.

†Electron-donor-acceptor complex

A term sometimes employed instead of charge transfer complex or Lewis adduct. Its use is discouraged.

See also adduct.

Electronation

A process that supplies an electron to a molecule or ion, i.e., electron transfer.

See reduction (1).

Electronegativity

A measure of the power of an atom or a group of atoms to attract electrons from other parts of the same molecular entity. The concept has been quantified by a number of authors, including especially Pauling and Mulliken.

See ATKINS (1974).

Electrophile, electrophilic

An "electrophilic reagent" or electrophile is a reagent that is preferentially attracted to a region of high electron density in a substrate. (Some radicals show weakly electrophilic behaviour).

In an "electrophilic substitution reaction" an electrophilic reagent is considered to effect heterolytic substitution in the other reactant both bonding electrons being supplied by that other reactant. For example,

$$C_6H_6 + \underset{\text{electrophilic reagent}}{NO_2^+} \longrightarrow C_6H_5NO_2 + \underset{\text{electrofuge}}{H^+}$$

"Electrophilic catalysis" is catalysis by a Lewis acid.

See also electrophilicity, nucleophilic.

Electrophilicity

The relative reactivity of an electrophilic reagent. (It is also sometimes referred to as "electrophilic power".) Qualitatively, the concept is related to Lewis acidity. However, whereas Lewis acidity is measured by relative equilibrium constants, electrophilicity is measured by relative rate constants for reactions of different electrophilic reagents towards a common substrate (usually involving attack at a carbon atom).

See also nucleophilicity.

Element effect

The element effect is said to be present in a given reaction series if there is a difference in the rate constant between substrates that differ only in the nature of the element of that atom in the leaving group by which the leaving group is attached to the rest of the molecular entity.

Elementary reaction

A one-step reaction or a reaction step that has no reaction intermediate.

See also stepwise reaction.

Elimination reaction

The reverse of an addition reaction.

See also α-elimination.

Enantioselectivity

See stereoselectivity.

Encounter complex

A complex of molecular entities produced at an encounter-controlled rate. When the complex is formed from two molecular entities it is called an "encounter pair". A distinction between (larger) encounter complexes and encounter pairs may be relevant in some cases, e.g., for mechanisms involving preassociation.

Encounter-controlled rate

A reaction rate corresponding to the rate of encounter of the reacting molecular entities (the chemical reaction occurring instantaneously on encounter). This is also known as a "diffusion-controlled rate" since rates of encounter are themselves controlled by diffusion rates (which in turn depend on the viscosity of the medium and the dimensions of the reactant molecular entities).

For a bimolecular reaction between solutes in water at 25°C an encounter-controlled rate is calculated to have a second—order rate constant of the order of 10^{10} dm^3 mol^{-1} s^{-1}.

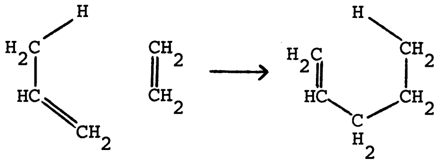
See also microscopic diffusion control, rate of reaction.

Encounter pair

See encounter complex.

Ene reaction

The addition of an olefin (or some other compound with a double bond) having an allylic hydrogen (the "ene") to a compound with a multiple bond (the "enophile") with transfer of the allylic hydrogen and a concomitant reorganization of bonding, as illustrated below for propene (the "ene") and ethylene (ethene; the "enophile"). The reverse process is a "retro-ene" reaction.



Energy of activation, E_a (Arrhenius energy of activation; activation energy)

An operationally defined quantity expressing the dependence of a rate constant on temperature according to

$$E_a = RT^2 \left(\frac{\partial \ln k}{\partial T}\right)_p$$

Derived from the "Arrhenius equation", $k = A \exp(-E_a/RT)$, where A is termed the "pre-exponential factor".

See also enthalpy of activation.

Energy profile

See Gibbs energy diagram, potential energy profile.

Enophile

See ene reaction.

Entering group

An atom or group that forms a bond to what is considered to be the main part of the substrate during a reaction. For example: the attacking nucleophile in a bimolecular nucleophilic substitution reaction.

See also leaving group.

Enthalpy of activation, $\Delta H^{\ddagger}$

The standard enthalpy difference between the transition state and the reactants at the same temperature and pressure.

It is related to the temperature coefficient of the reaction according to the equations

$$\Delta H^{\ddagger} = RT^2 \left(\frac{\partial \ln k}{\mathrm{d}T}\right)_p - RT$$

$$= E_a - RT$$

$$= - R\left(\frac{\partial \ln\ (k/T)}{\partial\ (1/T)}\right)_p$$

where E_a is the energy of activation, providing that rate constants for reactions other than first order reactions are expressed in temperature-independent concentration units (e.g., mol. dm^{-3}, measured at a fixed temperature and pressure). If $\ln k$ is expressed as $\ln k = (a/T)+b+c \ln T + dT$ then $\Delta H^{\ddagger} = - aR + (c-1)\ RT + dRT^2$. If the concentration units are mol dm^{-3} at the temperature of each experiment, the true and apparent enthalpy of activation differ by $(n\text{-}1/\alpha RT^2$, where n is the order of reaction and α the thermal expansivity.

Strictly speaking, the quantity defined is the enthalpy of activation at constant pressure, from which the enthalpy of activation at constant volume can be deduced.

See also entropy of activation, Gibbs energy of activation.

Entropy of activation, $\Delta S^{\ddagger}$

The standard entropy difference between the transition state and the reactants, at the same temperature and pressure.

It is related to Gibbs energy of activation and enthalpy of activation by the equations

$$\Delta S^{\ddagger} = (\Delta H^{\ddagger} - \Delta G^{\ddagger})/T$$

$$= \Delta H^{\ddagger}/T - R\ln(\underline{k}/h) + R\ln(k/T)$$

or, if $\ln k$ is expressed as $\ln k = a/T + b + c\ln T + dT$, $\Delta S^{\ddagger} = R[\ b + c - 1 - \ln(\underline{k}/h) + R(c-1)\ln T + 2dRT$,

provided that rate constants for reactions other than first-order reactions are expressed in temperature-independent concentration units (e.g., mol dm^{-3}, measured at a fixed temperature and pressure). The numerical value of $\Delta S^{\ddagger}$ depends on the standard state (and therefore on the concentration units) selected.

Strictly speaking, the quantity defined is the entropy of activation at constant pressure from which an entropy of activation at constnat volume can be deduced.

The information represented by the entropy of activation may alternatively be conveyed by the pre-exponential factor A (see energy of activation).

Equilibrium control

See thermodynamic control.

Equilibrium isotope effect

See isotope effect.

Excimer

An excited-state complex between an electronically excited molecular entity and an identical one in the ground state $[A + A^* \longrightarrow (A...A)^*]$

See also exciplex.

Exciplex

An excited state complex between an electronically excited molecular entity and a similar or dissimilar one in the ground state. $[A^* + B \longrightarrow (A...B)^*]$. The term "exciplex" is restricted to an excited complex of definite stoichiometry to distinguish it from a solvated excited molecule in which an indefinite number of unexcited solvent molcules form the environment of the elctronically excited molecular entity.

See also excimer.

External ion-pair return

The process that converts a loose ion pair into the corresponding covalent molecule via a tight ion pair.

$$R^+\|Z^- \longrightarrow R^+Z^- \longrightarrow RZ$$

loose ion pair   tight ion pair   covalent molecule

External ion-pair return is a special case of secondary geminate recombination.

See also external ion return, internal ion-pair return.

External ion return

The (reversible) process whereby dissociated ions go to loose ion pairs.

$$R^+ + Z^- \longrightarrow R^+\|Z^-$$

dissociated ions   loose ion pair

External return

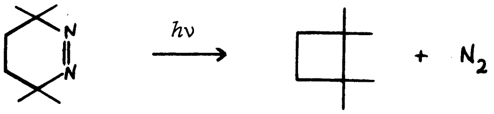
See external ion-pair return, external ion return.

Extrusion reaction

A reaction in which an atom or group Y connected to two other atoms or groups X and Z is lost from a molecule, leading to a product in which X is bonded to Z, e.g.,

$$X\text{-}Y\text{-}Z \longrightarrow X\text{-}Z + Y$$

or



The reverse of an extrusion reaction is called an insertion reaction.

Field effect

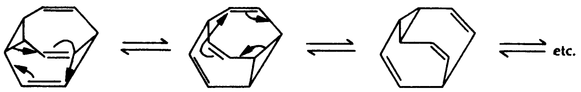
An experimentally observable effect (on reaction rates, etc.) of intramolecular coulombic interaction between the centre of interest and a remote pole or dipole, by direct action through space rather than through bonds. The magnitude of the field effect (or "direct effect") is dependent on the intensity, orientation, and shortest distance between the centre of interest and the remote pole or dipole. An approach to its calculation was described by KIRKWOOD and WESTHEIMER (1938).

See also inductive effect.

Fluxional

A fluxional chemical species undergoes rapid degenerate rearrangements (generally detectable only by spectroscopic line shape analysis).

Example:



Bullvalene
(10!/3 forms, valence tautomerism)

Fractionation factor (isotopic)

The ratio $(x_1/x_2)_A / (x_1/x_2)_B$, where x is the abundance, expressed as atom fraction, of the isotope distinguished by the subscript numeral, when the two isotopes are equilibrated between two different chemical species A and B (or between specific sites A and B in the same or in different chemical species). The term is most commonly met in connection with deuterium solvent isotope effects when the fractionation factor ϕ expresses the ratio $(x_D/x_H)_{solute}/(x_D/x_H)_{solvent}$ for the exchangeable hydrogen atoms in the chemical species (or sites) concerned.

Fragmentation

(1) The heterolytic cleavage of a molecule according to the general reaction a-b-c-d-X $\rightarrow$ a-b + c=d + :X, where a-b is an electrofuge and :X is a nucleofuge (which may emerge from the reaction in combined form), and the middle group c-d affords the unsaturated fragment c=d. For example,

$$Ph_3C.CO_2H + H^+ \longrightarrow Ph_3C^+ + CO + H_2O$$

GROB (1969).

(2) The breakdown of a radical into a diamagnetic molecule and a smaller radical, e.g., $X\text{-}Y\text{-}Z\cdot \rightarrow X{=}Y + Z\cdot$

(3) The breakdown of a radical ion in a mass spectrometer or in solution, forming an ion of lower molecular mass and a radical, e.g.,

$$[(CH_3)_3C\text{-}OH]^{+\cdot} \longrightarrow (CH_3)_2C{=}\overset{+}{O}H + .CH_3 \quad \text{(mass spectrometer)}$$

$$[ArBr]^{-\cdot} \longrightarrow Ar^{\cdot} + Br^- \quad \text{(solution)}$$

†Free energy ...

See Gibbs energy ...

This change conforms to the recommendations of IUPAC MANUAL (1979).

Free radical

See radical.

Frontier orbitals

The Highest-energy Occupied Molecular Orbital (HOMO) (filled or partly filled) and Lowest-energy Unoccupied Molecular Orbital (LUMO) (completely or partly vacant) of a molecular entity. Examination of the mixing of frontier orbitals of reacting molecular entities affords an approach to the interpretation of reaction behaviour; this constitutes a simplified perturbation molecular orbital theory of chemical behaviour.

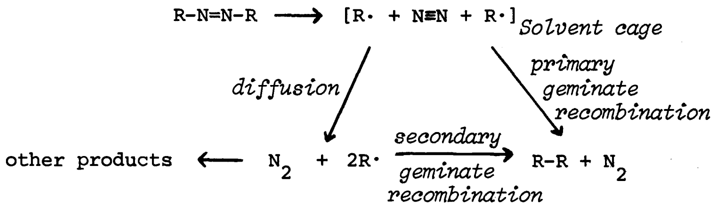
Geminate pair

See radical pair

Geminate recombination

The reaction with each other of two transient molecular entities produced from a common precursor in solution. If reaction occurs before any separation by diffusion has occurred, this is termed "primary geminate recombination". If the mutually reactive entities have been separated, and come together by diffusion, this is termed "secondary geminate recombination".

For example,



See also cage, external ion-pair return, internal ion-pair return.

General acid catalysis

The catalysis of a chemical reaction by a series of Brønsted acids, including the solvated hydrogen ion (the lyonium ion), so that the rate of the catalysed part of the reaction is given by $\sum_{HA} k_{HA}[HA]$ multiplied by some function of substrate concentrations. (The acids HA are unchanged by the overall reaction.) General acid catalysis can be experimentally distinguished from specific hydrogen-ion catalysis by observation of the reaction rate as a function of buffer concentration.

See also catalysis, catalytic constant, intramolecular catalysis, promotion, specific catalysis.

General base catalysis

The acceleration of a chemical reaction by a series of Brønsted bases, including the lyate ion, so that the rate of the catalysed part of the reaction is given by $\sum_{B} k_{B}[B]$ multiplied by some function of substrate concentrations.

See also general acid catalysis.

Gibbs energy diagram

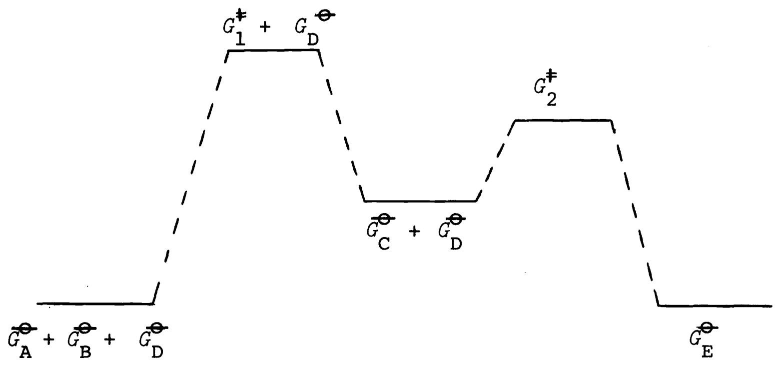
A diagram showing the relative standard Gibbs energies of reactants, transition states, reaction intermediates, and products in the same sequence as they occur in a chemical reaction. These points are often connected by a smooth curve (a "Gibbs energy profile", commonly still referred to as a "free energy profile") but experimental observation can provide information on relative standard Gibbs energies only at the maxima and minima and not at configurations between them. The abscissa expresses the sequence of reactants, products, reaction intermediates and transition states but is otherwise undefined.

Contrary to statements in many text books, the highest point on a Gibbs energy diagram does not necessarily correspond to the transition state of the rate-limiting step. For example, in a stepwise reaction consisting two reaction steps

$$A + B \rightleftharpoons C$$

$$C + D \longrightarrow E$$

one of the transition states of the two reaction steps must (in general) have a higher standard Gibbs energy than the other, whatever the concentration of D in the system. However, the value of that concentration will determine which of the reaction steps is rate-limiting.



See also potential energy profile, potential energy reaction surface.

Gibbs energy of activation, $\Delta G^{\ddagger}$ (Gibbs free energy of activation)

The standard Gibbs energy difference between the transition state of a reaction (either an elementary reaction or a stepwise reaction) and reactants. It is calculated from the experimental rate constant k via the conventional form of the absolute rate equation:

$$\Delta G^{\ddagger} = RT\ (\ln \underline{k}/h - \ln k/T)$$

where $\underline{k}$ is the Boltzmann constant and h the Planck constant ($\underline{k}/h = 2.08358 \times 10^{10}\ K^{-1}\ s^{-1}$) The values of rate constants, and hence Gibbs energies of activation, depend upon the choice of concentration units (or of the thermodynamic standard state).

See also entropy of activation.

Gibbs energy profile

See Gibbs energy diagram.

Group

A defined continuously linked collection of atoms within a molecular entity. This use of the term in physical organic and general chemistry differs from the more restrictive definition adopted for the purpose of nomenclature of organic compounds.
[See IUPAC ORGANIC RULES (1969), Section C]

See also substituent group.

Group electronegativity

See substituent electronegativity.

Grunwald-Winstein equation

The linear Gibbs energy relation

$$\lg\ (k_s/k_o) = mY$$

expressing dependence of the rate of solvolysis of a substrate on ionizing power of the solvent. The rate constant k_o applies to the reference solvent (ethanol-water, 80:20, v/v) and k_s to the solvent S, both at 25°. The parameter m is characteristic of the substrate and is assigned the value unity for *tert*-butyl chloride. The value Y is intended to be a quantitative measure of the ionizing power of the solvent S. The equation has also been applied to reactions other than solvolysis. (For the definition of other Y-scales, see BENTLEY and SCHLEYER (1977)].

GRUNWALD and WINSTEIN (1948); FAINBERG and WINSTEIN (1956).

See also polarity, Z-value.

Guest

An organic or inorganic ion or compound that forms a complex with (or occupies a cavity within the crystal structure of) a host molecule. Examples include molecular entities (especially ions) that form complexes with crown ethers or those that form clathrate complexes, or are enclosed in inclusion complexes.

Half-life

In a kinetic experiment, the time required for the concentration of a reactant to fall to one half of its initial value. (Its dependence on initial concentration depends upon the order of reaction. It is independent of initial concentration only for a first-order process.)

See also mean life-time.

Hammett acidity function

See acidity function.

Hammett equation (or Hammett relation)

See ρ-value.

Hammond principle (or Hammond postulate)

The hypothesis that, when a transition state leading to an unstable reaction intermediate (or product) has nearly the same energy as that intermediate, the two are interconverted with only a small reorganization of molecular structure. Essentially the same idea is sometimes referred to as "Leffler's assumption", namely, that the transition state bears the greater resemblance to the less stable species (reactant or reaction intermediate/product).

HAMMOND (1955); LEFFLER (1953).

Hard acid

A Lewis acid with an acceptor centre of low polarizability which preferentially associates with hard bases rather than with soft bases, in a qualitative sense. For example, hard acids prefer an O- (or N-) base to its S- (or P-) analogue.

See also soft acid.

Hard base

A Lewis base with a donor centre (e.g., an O atom) of low polarizability and with vacant orbitals of high energy. Hard bases associate preferentially with hard acids rather than with soft acids, in a qualitative sense.

See also soft base.

Heat capacity of activation, $\Delta C_p^{\ddagger}$

A quantity related to the temperature coefficient of $\Delta H^{\ddagger}$ (enthalpy of activation) and $\Delta S^{\ddagger}$ (entropy of activation) according to the equations:

$$\Delta C_p^{\ddagger} = \left(\frac{\partial \Delta H^{\ddagger}}{\partial T}\right)_p = T\left(\frac{\partial \Delta S^{\ddagger}}{\partial T}\right)_p$$

If the rate constant is expressible in the form $\ln k = a/T + b + c \ln T + dT$, then:

$$\Delta C_p^{\ddagger} = (c-1)R + 2dRT$$

See KOHNSTAM (1967).

Heteroconjugation

(1) Association between a base and the conjugate acid of a different base through a hydrogen bond ($\overset{+}{B}H...B'$ or $AH...A'^{-}$).

†(2) Some authors refer to "conjugated systems" containing a hetero-atom, e.g., pyridine, as "heteroconjugated systems". This usage is discouraged since it suggests an analogy to homoconjugation (2), which conflicts with the currently accepted definition of that term.

Heterolysis, heterolytic.

The cleavage of a bond so that both bonding electrons remain with one of the two fragments between which the bond is broken (e.g., $\overset{\curvearrowright}{A{-}B} \longrightarrow A^{+} + B^{-}$). Heterolysis of a bond (not forming part of a ring) in the unimolecular reaction of an electrically neutral molecular entity results in the formation of two oppositely charged ions (cf. homolysis).

Heterolytic bond fission is a feature of many bimolecular reactions in solution (e.g., electrophilic substitution, nucleophilic substitution).

See also heterolytic bond dissociation energy.

Heterolytic bond dissociation energy

The energy required to break a given bond of some specific compound by heterolysis. For the dissociation of a neutral molecule AB in the gas phase into A^+ and B^- the heterolytic bond dissociation energy $D(A^+B^-)$ is the sum of the bond dissociation energy, $D(A{-}B)$, and the adiabatic ionization energy of the radical A· *minus* the electron affinity of the radical B·.

Heterovalent hyperconjugation

See hyperconjugation.

Hofmann rule

"The principal olefin formed in the decomposition of quaternary ammonium hydroxides that contain different primary alkyl groups is always ethylene, if an ethyl group is present." Originally given in this limited form by A. W. Hofmann, the rule has since been extended and modified as follows: "When two or more alkenes can be produced in a β-elimination reaction, the alkene having the smallest number of alkyl groups attached to the double-bond carbon atoms will be the predominant product." The orientation described by the Hofmann rule is observed in elimination reactions of quaternary ammonium salts and tertiary sulfonium salts, and in certain other cases.

HOFMANN (1851).

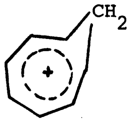
See also Saytzeff rule.

HOMO

See frontier orbitals.

Homoaromatic

Whereas in an aromatic molecule there is continuous overlap of p orbitals over a cyclic array of atoms, in a homoaromatic molecule there is a formal discontinuity in this overlap resulting from the presence of a single sp^3-hybridized atom within the ring; p orbital overlap apparently bridges this sp^3 centre, and features associated with aromaticity are manifest in the properties of the compound. Pronounced homoaromaticity is not normally associated with neutral molecules, but mainly with species bearing a formal electrical charge e.g., the "homotropylium" cation $C_8H_9^+$ (A)



(A)

In bis, tris-, (etc.) homoaromatic species, two, three, (etc.) single sp^3 centres separately interrupt the π-electron system.

See also homoconjugation (2).

Homoconjugation

(1) Association between a base and its conjugate acid through a hydrogen bond ($\overset{+}{B}H\ldots B$ or $AH\ldots A^-$)

(2) The orbital overlap of two π-systems separated by a non-conjugating group, such as CH_2.

See also homoaromatic.

Homolysis

The cleavage of a bond ("homolytic cleavage" or "homolytic fission") so that each of the molecular fragments between which the bond is broken retains one of the bonding electrons. A unimolecular reaction involving homolysis of a bond (not forming part of a cyclic structure) in a chemical species containing an even number of (paired) electrons results in the formation of two radicals ($\overset{\curvearrowleft\curvearrowright}{A\text{—}B} \longrightarrow A\cdot + B\cdot$) (cf. heterolysis), and is the reverse of colligation. Homolysis is also commonly a feature of bimolecular substitution reactions (and of other reactions) involving radicals and molecules.

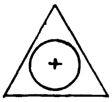
See also bond dissociation energy.

Host molecule

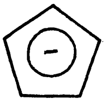
A molecule with convergent binding sites that forms complexes with organic or inorganic guests containing complementary binding sites, or that can accommodate guests within cavities of its crystal structure. (The adjective "convergent" here means that the additional bonds that can be formed at these sites would be directed towards a common central region or point.) Examples include crown ethers and macrocyclic molecules containing nitrogen, oxygen or sulfur (where these are ion-dipole attractions between the heteroatoms and positive ions), hydrogen-bonded molecules that form clathrates (e.g. hydroquinone and water), and host molecules of inclusion complexes (e.g. urea or thiourea). Van der Waals forces bind the guest to the host molecule in clathrates and inclusion complexes.

Hückel (4*n* + 2) rule

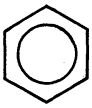
Monocyclic coplanar systems of trigonally hybridized atoms that contain (4*n* + 2)π-electrons (where *n* is an integer) will exhibit aromatic character. This rule is derived from the Hückel MO calculations on monocyclic conjugated hydrocarbons $(CH)_n$ according to which $(4n + 2)$ π-electrons are contained in a closed-shell system. Examples of systems that obey the Hückel rule include:



Cyclopropenyl
cation



Cyclopentadienyl
anion



Benzene

Systems containing $4n$ π-electrons (such as cyclobutadiene and the cyclopentadienyl cation) are "antiaromatic".

See also conjugation, Möbius aromaticity.

Hydration

Addition of the elements of water (i.e. H and OH) to a chemical species (cf. aquation). For example, hydration of ethylene (ethene):

$$H_2C{=}CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2OH$$

Hydrogen bond

The hydrogen bond is a form of association between an electronegative atom and a hydrogen atom attached to a second, relatively electronegative atom. Both electronegative atoms are usually (but not necessarily) from the first row of the periodic table, i.e., N,O, or F. Hydrogen bonds may occur inter- or intra-molecularly. They are, with a few exceptions, usually involving fluorine, no stronger than 20-25 kJ mol^{-1} (5-6 kcal mol^{-1}).

Hydrolysis

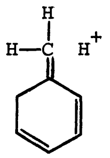
Solvolysis by water.

Hydrophobic interaction

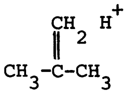
The tendency of hydrocarbons (or of lipophilic hydrocarbon-like groups in solutes) to form intermolecular or intramolecular aggregates in an aqueous medium. The name arises from the attribution of the phenomenon to the apparent repulsion between water and hydrocarbons. The misleading alternative term "hydrophobic bond" is discouraged.

Hyperconjugation

In the formalism that separates bonds into σ and π types, hyperconjugation is the interaction of a σ bond with a π network. This interaction is customarily illustrated by contributing structures, e.g. for toluene (below; sometimes said to be an example of "heterovalent" or "sacrificial hyperconjugation", so named because the contributing structure contains one two-electron bond less than the normal Lewis formula for toluene).



The concept of hyperconjugation is also extended to carbenium ions and radicals, where the interaction is now between a σ bond and un unfilled or partly filled π or p orbital. A contributing structure illustrating this for the *tert*-butyl cation is:



$$\begin{array}{c} CH_2\ H^+ \\ \| \\ CH_3{-}C{-}CH_3 \end{array}$$

This is sometimes called an example of "isovalent hyperconjugation" (the contributing structure containing the same number of two-electron bonds as the normal Lewis formula).

Both structures shown are also examples of "no-bond resonance".

Hypsochromic

See bathochromic.

Identity reaction

A chemical reaction whose products are chemically identical with the reactants.

See also degenerate rearrangement.

†Imene

See nitrene.

†Imidogen

See nitrene.

†Imidonium ion

See nitrenium ion.

†Imin

See nitrene.

†Imine radical

See nitrene.

Inclusion complex

A complex in which one component (the host molecule) forms a crystal lattice containing spaces in the shape of long tunnels or channels in which molecular entities of a second chemical species (the guest) are located. There is no bonding between guest and host compound, the attraction being generally due to van der Waals forces.

See also clathrate.

Inductive effect

An experimentally observable effect (on reaction rates, etc.) of the transmission of charge through a chain of atoms by electrostatic induction. Although the term has been taken by some authors to include the field effect, there is a theoretical distinction between these two effects as models for the coulombic interaction between a given site within a molecular entity and a remote pole or dipole within the same entity, and various methods of experimental distinction have been discussed. Some effects called "inductive" in the older literature are now considered to be field effects.

See also mesomeric effect.

†Inductomeric effect (obsolescent)

A molecular polarizability effect occurring by the inductive mechanism of electron displacement.

See INGOLD (1953).

Inert

Stable and unreactive.

Inhibition

The decrease in rate of reaction brought about by the addition of a substance (inhibitor), by virtue of its effect on the concentration of a reactant, catalyst or reaction intermediate. For example, molecular oxygen and *p*-benzoquinone can act as "inhibitors" in many reactions involving radicals as intermediates by virtue of their ability to act as scavengers towards these radicals.

If the rate of a reaction in the absence of inhibitor is v_o and that in the presence of a certain amount of inhibitor is v, the degree of inhibition (i) is given by

$$i = (v_o - v)/v_o$$

Initiation

A reaction or process generating free radicals (or some other reactive reaction intermediates) which then participate in a chain reaction. For example, in the chlorination of alkanes by a radical mechanism the initiation step is the dissociation of molecular chlorine.

Insertion reaction

A chemical reaction of the general type

$$\text{X-Z} + \text{Y} \longrightarrow \text{X-Y-Z}$$

in which a connecting atom or group Y replaces the bond joining the parts X and Z of the reactant XZ. An example is the carbene insertion reaction

$$R_3C\text{-}H + CH_2 \longrightarrow R_3C\text{-}CH_3$$

The reverse of an insertion reaction is called an extrusion reaction.

Intermediate

See reaction intermediate.

Intermolecular

(1) Descriptive of any process that involves the transfer of atoms, groups, electrons, etc. or of interactions between molecular entities.

(2) Relating to a comparison between different molecular entities.

See also intramolecular.

Internal ion-pair return

The direct conversion of a tight ion pair into the related covalent species without the prior separation of the ions into a loose ion pair:

$$R^+Z^- \longrightarrow R\;Z$$

R^+Z^-	RZ
tight ion pair	covalent molecule

It is a special case of primary geminate recombination.

See also external ion-pair return.

Internal return

See internal ion-pair return, external ion-pair return.

Intimate ion pair

See ion pair.

Intramolecular

(1) Descriptive of any process that involves a transfer (of atoms, groups, electrons, etc.) or of interactions between different parts of the same molecule (or molecular entity).

(2) Relating to a comparison between atoms or groups within the same molecular entity.

See also intermolecular.

Intramolecular catalysis

The acceleration of a chemical transformation at one site of a molecular entity through involvement of another functional ("catalytic") group in the same molecular entity, without that group appearing to have undergone change in the reaction product. The use of the term should be restricted to cases for which analogous intermolecular catalysis by chemical species bearing that catalytic group is observable. Intramolecular catalysis can be detected and expressed in quantitative form by a comparison of the reaction rate with that of a strictly comparable model compound in which the catalytic group is absent, or by measurement of the effective molarity of the catalytic group.

See also neighbouring-group participation.

Inverse kinetic isotope effect

See isotope effect.

Inverse micelle

See inverted micelle.

Inverted micelle

The reversible formation of association colloids from surfactants in non-polar solvents leads to aggregates termed inverted (or inverse, reverse, or reversed) micelles. Such association is often of the type

$$\text{Monomer} \rightleftharpoons \text{Dimer} \rightleftharpoons \text{Trimer} \rightleftharpoons \cdots\cdots \rightleftharpoons n\text{-mer}$$

and the phenomenon of critical micelle concentration (or an analogous effect) is consequently not observed.

In an inverted micelle the polar groups of the surfactants are concentrated in the interior and the lipophilic groups extend towards and into the non-polar solvent.

Ion pair

A pair of oppositely charged ions held together by coulombic attraction without formation of a covalent bond. Experimentally, an ion pair behaves as one unit in determining conductivity, kinetic behaviour, osmotic properties, etc.

Following Bjerrum, oppositely charged ions with their centres closer together than a distance $q = (8.36 \times 10^6\ z_+z_- / \varepsilon_r T)$ pm are considered to constitute an ion pair ("Bjerrum ion pair"). [z_+z_- are the charges of the ions, and ε_r is the relative permittivity (or dielectric constant) of the medium.]

An ion pair, the constituent ions of which are in direct contact (and not separated by an intervening solvent or other neutral molecule), is designated as a "tight ion pair" (or "contact ion pair"). A tight ion pair of X^+ and Y^- is symbolically represented as X^+Y^-.

By contrast, an ion pair whose constituent ions are separated by one or several solvent or other neutral molecules is described as a "loose ion pair", symbolically represented as $X^+ \| Y^-$. The members of a loose ion pair can readily interchange with other free or loosely paired ions in the solution. This interchange may be detectable (e.g., by isotopic labelling) and thus afford an experimental distinction between tight and loose ion pairs.

A further conceptual distinction has sometimes been made between two types of loose ion pairs. In "solvent-shared ion pairs" the ionic constituents of the pair are separated by only a single solvent molecule, whereas in "solvent-separated ion pairs" more than one solvent molecule intervenes. However, the term "solvent-separated ion pair" must be used and interpreted with care since it has also widely been used as a less specific synonym for "loose ion pair".

See also common-ion effect, dissociation, external ion return, external ion-pair return, internal ion-pair return.

Ionization

The generation of one or more ions. It may occur, e.g., by loss of an electron from a neutral chemical species, by the unimolecular heterolysis of such a species into two or more ions, or by a heterolytic substitution reaction involving neutral molecules, such as

$$CH_3CO_2H + H_2O \rightarrow H_3O^+ + CH_3CO_2^-$$

and $$Ph_3CCl + AlCl_3 \rightarrow Ph_3C^+ + AlCl_4^-$$

The loss of an electron from a singly, doubly, etc. charged cation is called second, third, etc. ionization. This terminology is used especially in mass spectrometry.

See also ionization energy.

Ionization energy

The minimum energy (enthalpy) required to remove an electron from an isolated molecular entity (in its vibrational ground state) in the gaseous phase. If the resulting molecular entity is considered to be in its vibrational ground state, one refers to the energy as the "adiabatic ionization energy". If the molecular entity produced possesses the vibrational energy determined by the Franck-Condon principle (according to which the electron ejection takes place without an accompanying change in molecular geometry), the energy is called the "vertical ionization energy". The name ionization energy is preferred to the somewhat misleading earlier name "ionization potential".

See also ionization.

† Ionization potential

See ionization energy.

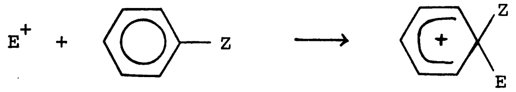
Ionizing power

A qualitative term to denote the tendency of a particular solvent to promote ionization of an uncharged solute. The term has been used both in a kinetic and in a thermodynamic context.

See also Grunwald-Winstein equation.

Ipso-Attack

The attachment of an entering group to a position in an aromatic compound already carrying a substituent group (other than hydrogen). The entering group may displace that substituent group but may also itself be expelled or migrate to a different position in a subsequent step. For example,



where E^+ is the electrophile and Z is a substituent (other than hydrogen).

Isoentropic

A reaction series is said to be isoentropic if the individual reactions of the series have the same entropy of activation.

Isokinetic relationship

If a series of structurally related substrates undergo the same general reaction, the enthalpies and entropies of activation sometimes satisfy the relation

$$\Delta H^{\ddagger} - \beta \Delta S^{\ddagger} = \text{constant}$$

where the parameter β is independent of temperature. This equation (or some equivalent form) is said to represent an "isokinetic relationship". The temperature $T = \beta$ (at which all substrates of a series obeying the isokinetic relationship react at the same rate) is termed the "isokinetic temperature".

See LEFFLER (1955).

Isomerization

A chemical reaction, the principal product of which is isomeric with the principal reactant. An intramolecular isomerization that involves the breaking and making of bonds is a special case of a molecular rearrangement. Isomerization does not necessarily imply molecular rearrangement (e.g., in the case of the interconversion of conformational isomers).

Isosbestic point

The absorption spectra (or curves of absorbance against wavelength or frequency) of two chemical species will intersect at wavelengths at which the molar absorption coefficients (formerly called "extinction coefficients") of the species are equal. All mixtures (or solutions) of two such species, having the same total concentration, will then exhibit absorption spectra that pass through the same intersections (called isosbestic points), provided the component species do not interact. Isosbestic points will also be observable in systems where the two non-interacting components (considered in the foregoing to be single chemical species) are themselves mixtures (of fixed composition) of several species.

Isosbestic points are, for instance, found in the spectra of an acid-base indicator for which a single conjugate acid-base pair of forms is present in the solution, or in the spectra traced during the course of a reaction in which reactant is converted to product in a quantitative reaction, without significant build-up in the concentration of any reaction intermediate.

The term is most commonly used in the context of electronic spectroscopy.

Isotope effect

The ratio of the rate or equilibrium constants of two reactions that differ only in the isotopic composition of one or more of their otherwise chemically identical components, i.e. $k_{\text{light}}/k_{\text{heavy}}$ ("kinetic isotope effect") and $K_{\text{light}}/K_{\text{heavy}}$ ("equilibrium isotope effect"). The use of the reciprocal ratios to express isotope effects is discouraged.

A distinction can be made between intermolecular isotope effects (when a comparison is made between isotopically different reactant molecular entities) and intramolecular isotope effects (when the different isotopes occupy chemically equivalent alternative reactive sites within the same molecular entity, so that the reaction results in isotopically distinguishable products).

A kinetic isotope effect is termed "normal" or "inverse" according to whether $k_{\text{light}}/k_{\text{heavy}}$ is larger or smaller than unity. (The use of the term "normal" must not be interpreted too literally: inverse isotope effects are the "norm" for certain types of reaction.)

The absence of isotopic discrimination for rate or equilibrium constants ($k_{\text{light}}/k_{\text{heavy}} = 1$ or $K_{\text{light}}/K_{\text{heavy}} = 1$) is, strictly speaking, a "unity isotope effect". It is more commonly thought of as a "null isotope effect", on the grounds that there is zero isotopic effect on the corresponding standard Gibbs energy change, i.e. that an isotope *effect* exists only when the ratio of rate or equilibrium constants differs from unity.

A kinetic isotope effect attributable to isotopic substitution of an atom to which a bond is made or broken in the rate-limiting step or in a pre-equilibrium step of a specified reaction is termed a "primary kinetic isotope effect". For example, $k_B/k_{B'}$ is the primary kinetic isotope effect for the reactions

$$\text{A-B} + \text{C} \xrightarrow{k_B} \text{A} + \text{B-C}$$

$$\text{A-B'} + \text{C} \xrightarrow{k_{B'}} \text{A} + \text{B'-C}$$

where B and B' are the light and heavy isotopes, respectively. The corresponding isotope effect on the equilibrium constant of such a reaction is called a "primary equilibrium isotope effect".

A kinetic isotope effect attributable to isotopic substitution of an atom to which bonds are neither made nor broken in the rate-limiting step or in a pre-equilibrium of a specified reaction is termed a "secondary kinetic isotope effect". For example, $k_D/k_{D'}$ is the secondary kinetic isotope effect for the reactions:

$$\text{D-A-B} + \text{C} \xrightarrow{k_D} \text{D-A} + \text{B-C}$$

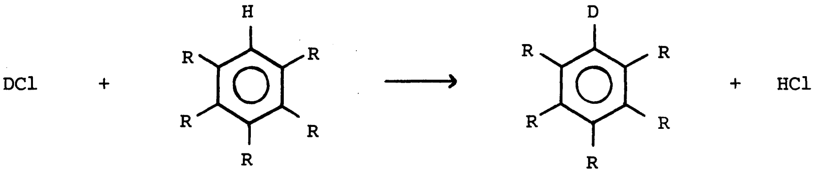
$$\text{D'-A-B} + \text{C} \xrightarrow{k_{D'}} \text{D'-A} + \text{B-C}$$

where D and D' are the light and heavy isotopes, respectively. One speaks of α, β (etc.) secondary isotope effects where α, β (etc.) denote the position of isotopic substitution relative to the reaction centre. The corresponding isotope effect on the equilibrium constant of such a reaction is called a "secondary equilibrium isotope effect".

A "solvent isotope effect" is any kinetic or equilibrium isotope effect resulting from a change in the isotopic composition of the solvent.

Isotope exchange

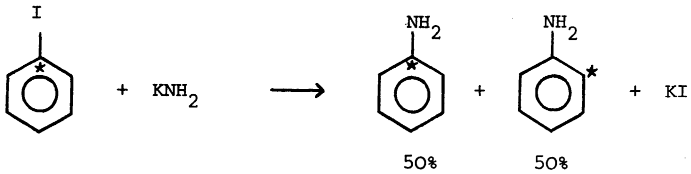
A reaction in which the reactant and product molecules are chemically identical but have different isotopic composition. In such a reaction the isotope distribution tends towards equilibrium (as expressed by fractionation factors) as a result of transfers of isotopically different atoms or groups. For example,



Isotopic scrambling

The approach to or achievement of an equilibrium distribution of isotopes within a specified set of atoms in a chemical species or group of chemical species. For example,

(a)



(b) $(Ph\overset{*}{N}\equiv N)^{+} \longrightarrow (Ph\overset{*}{N}\equiv N)^{+} + (PhN\equiv\overset{*}{N})^{+}$

(*denotes position of an isotopically different atom)

See also fractionation factor.

Isovalent hyperconjugation

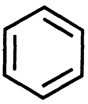
See hyperconjugation.

Kekulé structure (for aromatic compounds)

One of the contributing structures of an aromatic chemical species (such as benzene), with fixed alternating single and double bonds.

For benzene,

and



are the Kekulé structures.

Kinetic control (of product composition)

The term characterizes conditions that lead to reaction products in a proportion determined only by the relative rates of the parallel (forward) reactions leading to their formation. For example, the proportion of isomers formed in the nitration of chlorobenzene by nitric acid-sulfuric acid is determined by kinetic control.

See also thermodynamic control.

Kinetic electrolyte effect (kinetic ionic strength effect)

The general effect of an added electrolyte (i.e., an effect other than, or in addition to, that due to its possible involvement as a reactant or catalyst) on the observed rate constant of a reaction in solution. At low concentrations (when only long-range coulombic forces need to considered) the effect on a given reaction is determined only by the ionic strength $I = \frac{1}{2}\sum_{i} c_i z_i^2$ (c_i = concentration, z_i = charge, for ion i) of the solution and not by the chemical identity of the ions. For practical purposes, this concentration range is roughly the same as the region of validity of the Debye-Hückel limiting law for activity coefficients. At higher concentrations, the effect of an added electrolyte depends also on the chemical identity of the ions. Such specific action can usually be interpreted as the incursion of reaction paths involving an ion of the electrolyte as reactant or catalyst, in which case the action is not properly to be regarded just as a kinetic electrolyte effect.

Kinetic electrolyte effects are sometimes (too restrictively and therefore incorrectly) referred to as kinetic "salt effects".

A kinetic electrolyte effect ascribable solely to the influence of the ionic strength on activity coefficients of ionic reactants and transition states is called "a primary kinetic electrolyte effect".

A kinetic electrolyte effect arising from the influence of the ionic strength of the solution upon the pre-equilibrium concentration of an ionic species that is involved in a subsequent rate-limiting step of a reaction is called a "secondary kinetic electrolyte effect". A common case encountered in practice is the effect on the concentration of hydrogen ion (acting as catalyst) produced from the ionization of a weak acid in a buffer solution.

Kinetic equivalence

Two reaction schemes are kinetically equivalent if they imply the same orders of reaction for all chemical species involved.

For example, consider the two schemes (i) and (ii) for the formation of C from A:

$$\text{(i)} \quad A \underset{k_{-1},\ OH^-}{\overset{k_1,\ OH^-}{\rightleftharpoons}} B \xrightarrow{k_2} C$$

Providing that B does not accumulate as a reaction intermediate

$$\frac{d[C]}{dt} = \frac{k_1 k_2\,[A][OH^-]}{k_2 + k_{-1}[OH^-]} \qquad \text{.... (1)}$$

$$\text{(ii)} \quad A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow[OH^-]{k_2} C$$

Providing that B does not accumulate as an intermediate

$$\frac{d[C]}{dt} = \frac{k_1 k_2[A][OH^-]}{k_{-1} + k_2[OH^-]} \qquad \text{.... (2)}$$

Both equations for $d[C]/dt$ are of the form:

$$\frac{d[C]}{dt} = \frac{r[A][OH^-]}{1 + s[OH^-]} \qquad \text{.... (3)}$$

where r and s are constants. They are identical in their dependence on concentrations, and do not distinguish whether OH^- is required to catalyse the formation of B or its further transformation to C. The two schemes are therefore kinetically equivalent.

Kinetic isotope effect

See isotope effect.

Kosower *Z*-value

See *Z*-value.

Labile

The term has loosely been used to describe either a relatively unstable and transient chemical species or (less commonly) a relatively stable but reactive species. It must therefore not be used without explanation of the intended meaning, and is best avoided altogether.

Least motion (Principle of)

The hypothesis that, for given reactants, the reactions involving the smallest change in atomic positions will have the lowest energy of activation.

See HINE (1977).

Leaving group

An atom or group (charged or uncharged) that becomes detached from an atom in what is considered to be the residual or main part of the substrate in a specified reaction.

For example, in the heterolytic solvolysis of benzyl bromide in acetic acid

$$PhCH_2Br + AcOH \longrightarrow PhCH_2OAc + HBr$$

the leaving group is Br^-; in the reaction

$$MeS^- + PhCH_2\overset{+}{N}Me_3 \longrightarrow MeSCH_2Ph + Me_3N$$

it is Me_3N; in the electrophilic nitration of benzene, it is H^+. The term has meaning only in relation to a specified reaction. The leaving group is not, in general, the same as the substituent group present in the substrate (e.g., bromine and trimethylammonio in the substrates of the first two examples above).

See also electrofuge, entering group, nucleofuge.

Leffler's assumption

See Hammond principle.

Levelling effect

The tendency of a solvent to make all Brønsted acids whose acidity exceeds a certain value appear equally acidic. It is due to the complete transfer to a protophilic solvent of a proton from a dissolved acid stronger than the conjugate acid of the solvent. The only acid present to any significant extent in all such solutions is the lyonium ion. For example, the solvent water has a levelling effect on the acidities of $HClO_4$, HCl, and HI: aqueous solutions of these acids at the same (moderately low) concentrations have the same acidities. A corresponding levelling effect applies to strong bases in protogenic solvents.

Lewis acid

A chemical species that is an electron-pair acceptor and therefore able to react with a Lewis base to form a Lewis adduct, by sharing the electron pair furnished by the Lewis base. For example:

$$\underset{\text{Lewis acid}}{Me_3B} \quad + \quad \underset{\text{Lewis base}}{:NH_3} \longrightarrow \underset{\text{Lewis adduct}}{Me_3\overset{-}{B}-\overset{+}{N}H_3}$$

See also co-ordination, dipolar bond.

Lewis acidity

The thermodynamic tendency of a substance to act as a Lewis acid. Comparative measures of this property are provided by the equilibrium constants for Lewis adduct formation for a series of Lewis acids with a common reference Lewis base.

See also electrophilicity.

Lewis adduct

The adduct formed between a Lewis acid and a Lewis base.

Lewis base

A chemical species able to provide a pair of electrons and thus capable of co-ordination to a Lewis acid, thereby producing a Lewis adduct.

Lewis basicity

The thermodynamic tendency of a substance to act as a Lewis base. Comparative measures of this property are provided by the equilibrium constants for Lewis adduct formation for a series of Lewis bases with a common reference Lewis acid.

See also nucleophilicity.

Lewis formula (electron dot or Lewis structure)

Molecular structures in which the valency electrons are shown as dots so placed that one pair of dots represents two electrons or one (single) covalent bond between two atoms, e.g. $H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$ A double bond is represented by two pairs of dots, etc. Non-bonded electrons are placed adjacent to the atoms with which they are associated. Formal charges (e.g. +, −, 2+, etc.) are attached to atoms to indicate the difference between the positive nuclear charge (atomic number) and the total number of electrons (including those in inner shells), on the formal basis that bonding electrons are shared equally between the atoms they join. (Bonding pairs of electrons are sometimes denoted by lines, representing bonds, as in line formulae.)

Life-time

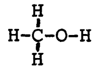
See mean life-time, half-life.

Ligand

If it is possible to indicate a "central" atom in a polyatomic chemical species, the atoms or groups bound to that atom are called ligands. (cf. IUPAC INORGANIC RULES (1970); Rule 2.24). The term is generally used in connection with metallic "central" atoms.

Line formula

A two-dimensional representation of molecular entities in which atoms are shown joined by lines representing single bonds, without any indication or implication of stereochemistry. For example, methanol is represented as



$$\begin{array}{c} H \\ | \\ H\text{-}C\text{-}O\text{-}H \\ | \\ H \end{array}$$

Such formulae are also known as "Couper-Butlerow structures".

(The term should not be confused with the representation of chemical formulae by the "Wiswesser line notation", a method of string notation. Formulae in this notation are also known as "Wiswesser line formulae".)

Linear Gibbs energy relation

A linear correlation between the logarithm of a rate constant or equilibrium constant for one series of reactions with the logarithm of the rate constant or equilibrium constant for a related series of reactions. Typical examples of such relations (frequently still known as "linear free energy relations") are the Brønsted relation, and the Hammett $\rho\sigma$ equation (see ρ-value).

The name arises because the logarithm of an equilibrium constant (at constant temperature and pressure) is proportional to a standard Gibbs energy change, and the logarithm of a rate constant is a linear function of a Gibbs energy of activation.

Lineweaver-Burk plot

See Michaelis-Menten kinetics.

Lipophilic

Literally, "fat-loving". Applied to molecular entities (or parts of molecular entities) having a tendency to dissolve in fat-like (i.e. hydrocarbon) solvents.

See also hydrophobic interaction.

Loose ion pair

See ion pair.

LUMO

See frontier orbitals.

Lyate ion

The anionic product of the autoprotolysis of a protogenic solvent, also produced by dissolving a Brønsted base in that solvent. For example, the hydroxide ion is the lyate ion of water.

Lyonium ion

The cation produced by protonation of a solvent molecule. For example, $CH_3OH_2^+$ is the lyonium ion in methanol solution.

Macroscopic diffusion control

The limitation of the rate of reaction for a reaction in solution by the rate of mixing by diffusion of solutions of the two reactants. It can occur even when the reaction rate constant is several powers of ten less than for an encounter-controlled rate. Analogous (and even more important) effects of the limitation of reaction rates by the speed of mixing are encountered in heterogeneous (solid/liquid, solid/gas, liquid/gas) systems.

See also microscopic diffusion control.

"Magic acid"

See superacid.

Markovnikov rule

"In the addition of hydrogen halides to olefins, the halogen atom becomes attached to the carbon bearing the lesser number of hydrogen atoms." Originally formulated by V. Markovnikov to generalize the orientation in additions of hydrogen halides to simple alkenes, this rule has been extended to polar addition reactions as follows. "In the heterolytic addition of a polar molecule to an alkene or alkyne, the more electronegative atom (or part) of the polar molecule becomes attached to the carbon atom bearing the smaller number of hydrogen atoms." This rule has also been cast in semi-mechanistic terms as stating that the more electropositive part of the polar molecule becomes attached to the end of the multiple bond that would result in the more stable carbenium ion (whether or not a carbenium ion is actually formed as a reaction intermediate in the addition reaction). Addition in the opposite sense may occur when the reaction involves homolysis of the polar molecule, and is commonly called "anti-Markovnikov addition".

MARKOVNIKOV (1870).

Mean life-time

For a given chemical species in a system at equilibrium the mean life-time is the average time spent in a specified state. In any process without overall chemical change the mean life-time, τ, which governs, and can be measured by, spectral line broadening is given by:

$$\tau = \frac{\text{Number of molecules in a specified state}}{\text{Number of molecules leaving that state per unit time}}$$

For a reactant undergoing a first-order decomposition, τ is the time taken for the concentration to fall to $1/e$ of its initial value ($e = 2.718$). The mean life-time is then equal to the reciprocal of the sum of rate constants for all concurrent first-order decompositions, i.e. $\tau = 1/\Sigma k$.

See also half-life.

Mechanism

A detailed description of the pathway leading from the reactants to the products of a reaction, including as complete a characterization as possible of the composition, structure, and other properties of reaction intermediates and transition states. An acceptable mechanism of a specified reaction (and there may be a number of such alternative mechanisms not excluded by the evidence) must be consistent with the reaction stoichiometry, the rate law, and with all other available experimental data, such as the stereochemical course of the reaction. Inferences concerning the electronic and nuclear motions which dynamically interconvert successive species along the reaction path (as represented by curved arrows, for example) are often included in the description of a mechanism.

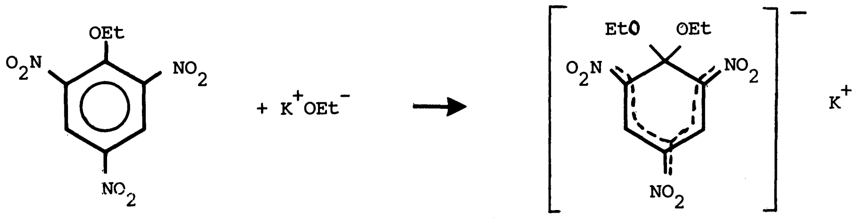
See also Gibbs energy diagram.

Medium

The phase (and composition of the phase) in which chemical species and their reactions are studied in a particular investigation.

Meisenheimer adduct

A cyclohexadienyl derivative formed as Lewis adduct from a nucleophile (Lewis base) and an aromatic or heteroaromatic compound. In earlier usage the term "Meisenheimer complex" was restricted to the typical Meisenheimer alkoxide adducts of nitro-substituted aromatic ethers, e.g.,



See also σ-adduct.

Mesomeric effect

The experimentally observable effect (on reaction rates, etc.) of a substituent due to the overlap of its p- or π-orbital with the p- or π-orbitals of the rest of the molecular entity. Mesomerism (or resonance) is thereby introduced or extended, and electronic charge may flow to or from the substituent.

See also field effect, inductive effect.

See INGOLD (1953).

Mesomerism

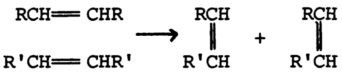
Essentially synonymous with resonance. Particularly associated with the picture of π-electrons as less localized in an actual molecule than in a Lewis formula.

The term is intended to imply that the correct representation of a structure is intermediate between two or more Lewis formulae.

See also delocalization.

Metathesis

A bimolecular process formally involving the exchange of a bond (or bonds) between chemically similar interacting species such that the bonding affiliations in the products are identical (or closely similar) to those in the reactants. For example:



$$\begin{matrix} \mathrm{RCH{=}CHR} \\ \mathrm{R'CH{=}CHR'} \end{matrix} \longrightarrow \begin{matrix} \mathrm{RCH} \\ \| \\ \mathrm{R'CH} \end{matrix} + \begin{matrix} \mathrm{RCH} \\ \| \\ \mathrm{R'CH} \end{matrix}$$

(The term has its origin in inorganic chemistry but this older usage is not applicable in organic chemistry.)

Methylene

See carbene.

Methylidyne

See carbyne.

Micellar catalysis

The acceleration of a reaction in solution by the addition of a surfactant so that the reaction can proceed in the environment of surfactant aggregates. (Rate enhancements may be due to one or more of the following: higher concentration of reactants in that environment, more favourable orientation and solvation of the species, enhanced rate constants in the micellar pseudophase of the surfactant aggregate.)

Micelle

See IUPAC MANUAL APPENDIX II (1972).

Michaelis-Menten kinetics

The dependence of an initial rate of reaction upon the concentration of a substrate [S] that is present in large excess over the concentration of an enzyme or other catalyst (or reagent) E with the appearance of saturation behaviour following the Michaelis-Menten equation,

$$v = V_m[S]/(K_m + [S]),$$

where v is the observed initial rate, V_m is the maximum initial rate at substrate saturation (i.e., $[S] \gg K_m$), and K_m the substrate concentration when $v = V_m/2$. The definition is experimental, i.e. it applies to any reaction that follows an equation of this general form.

The parameters V_m and K_m (the "Michaelis constant") of the equation can be evaluated from the slope and intercept of a linear plot of v^{-1} against $[S]^{-1}$ (a "Lineweaver-Burk plot").

A Michaelis-Menten equation is also applicable to the less usual condition where E is present in large excess, in which case the concentration [E] appears in the equation instead of [S].

Less correctly, the term has sometimes been used to describe reactions that proceed according to the scheme

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_{cat}} \text{Products}$$

in which case $K_m = (k_{-1} + k_{cat})/k_1$ (Briggs-Haldane conditions). It has also been used to describe only the special case in which $k_{-1} \gg k_{cat}$ and $K_m = k_{-1}/k_1 = K_s$; in this case K_m is a true dissociation constant (Michaelis-Menten conditions).

Microscopic diffusion control (encounter control)

The observable consequence of the limitation that the rate of a chemical reaction in a homogeneous medium cannot exceed the rate of encounter of the reacting molecular entities.

If (hypothetically) a bimolecular reaction in a homogeneous medium occurred instantaneously when two reactant molecular entities made an encounter, the rate of the reaction would be an encounter-controlled rate, determined solely by rates of diffusion of the reactants. Such a hypothetical "fully diffusion-controlled rate" is also said to correspond to "total microscopic diffusion control", and represents the asymptotic limit of the rate of reaction as the rate constant for the chemical conversion of the encounter pair into product (or products) becomes infinitely large.

"Partial microscopic diffusion control" is said to operate in a homogeneous reaction when the rates of chemical conversion and of encounter are comparable. (The degree of microscopic diffusion control cannot usually be determined with any precision.)

See also macroscopic diffusion control.

Microscopic reversibility, (Principle of)

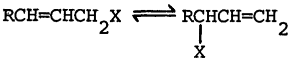
"At equilibrium, any molecular process occurs with the same frequency as the reverse of that process."

See also detailed balancing.

Migration

(1) The (usually intramolecular) transfer of an atom or group during the course of a molecular rearrangement.

(2) The movement of a bond to a new position, within the same molecular **entity**, is known as "bond migration". Allylic rearrangements, e.g.,



$$RCH{=}CHCH_2X \rightleftharpoons RCH(X)CH{=}CH_2$$

exemplify both types of migration.

Möbius aromaticity

A monocyclic array of orbitals in which there is a single out-of-phase overlap (or, more generally, an odd number of out-of-phase overlaps) reveals the opposite pattern of aromatic character to Hückel systems; with $4n$ electrons it is stabilized (aromatic), whereas with $4n + 2$ it is destabilized (antiaromatic). No examples of ground state Möbius systems are known, but the concept has been applied to transition states of pericyclic reactions [see aromatic (3)]. The name is derived from the topological analogy of such an arrangement of orbitals to a Möbius strip.

HEILBRONNER (1964), ZIMMERMAN (1971).

See also Hückel ($4n + 2$) rule.

Molecular entity

Any chemically or isotopically distinct atom, molecule, ion, ion pair, radical, radical ion, complex, conformer etc., capable of existence as a separately distinguishable entity.

See also chemical species.

Molecular orbital

A one-electron wave function describing an electron moving in the effective field provided by the nuclei and all other electrons of a molecular entity of more than one atom. Such molecular orbitals can be transformed in prescribed ways into component functions to give "localized molecular orbitals". Molecular orbitals can also be described, in terms of the number of nuclei (or "centres") encompassed, as two-centre, multi-centre, etc., molecular orbitals.

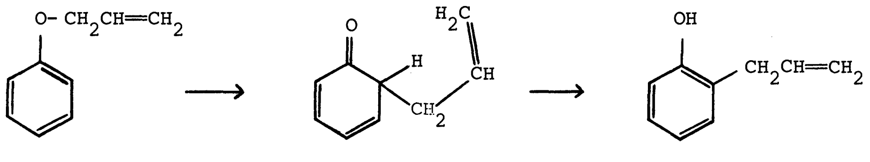
An orbital is usually depicted by sketching contours on which the wave function has a constant value (contour map) or by indicating schematically the envelope of the region of space in which there is an arbitratily fixed high (say 95%) probability of finding the electrons occupying the orbital, giving also the algebraic sign (+ or -) of the wave function in each part of that region.

Molecular rearrangement

A chemical reaction that contains a rearrangement stage.

The term is traditionally applied to any reaction that violates the so-called "principle of minimum structural change". According to this over-simplified hypothesis, chemical species do not isomerize, and the transformation of a functional group of a chemical species into a different functional group does not involve the making or breaking of more than the minimum number of bonds required to effect that transformation. For example, any new substituents should enter the precise positions previously occupied by displaced groups.

The simplest type of rearrangement is an intramolecular reaction in which the product is isomeric with the reactant (one type of "intramolecular isomerization"). An example is the first step of the Claisen rearrangement:



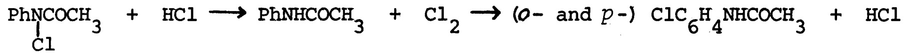
The definition of molecular rearrangement also includes changes in which there is a migration of an atom or bond (unexpected on the basis of the principle of minimum structural change), as in the reaction

$$CH_3CH_2CH_2Br \quad + \quad AgOAc \longrightarrow (CH_3)_2CHOAc \quad + \quad AgBr$$

where the rearrangement stage can formally be represented as the "1,2-shift" of hydride between adjacent carbon atoms in the carbenium ion $(CH_3CH_2\overset{+}{C}H_2 \longrightarrow CH_3\overset{+}{C}HCH_3)$ as well as reactions in which an entering group takes up a different position from the leaving group, with accompanying bond migration. An example of the latter type is the "allylic rearrangement":

$$(CH_3)_2C{=}CHCH_2Br \quad + \quad OH^- \longrightarrow (CH_3)_2C(OH)CH{=}CH_2 \quad + \quad Br^-$$

A distinction is made between "intramolecular rearrangements" (or "true molecular rearrangements") and "intermolecular rearrangements" (or "apparent rearrangements"). In the former case the atoms and groups that are common to a reactant and a product never separate into independent fragments during the rearrangement stage (i.e., the change is intramolecular), whereas in an "intermolecular rearrangement" a migrating group is completely free from the parent molecule and is reattached at a different position in a subsequent step, as in the Orton reaction:



$$\mathrm{Ph\underset{\displaystyle Cl}{N}COCH_3} + \mathrm{HCl} \longrightarrow \mathrm{PhNHCOCH_3} + \mathrm{Cl_2} \longrightarrow (o\text{- and } p\text{-})\ \mathrm{ClC_6H_4NHCOCH_3} + \mathrm{HCl}$$

Molecularity

The number of separate molecular entities that come together in an elementary reaction and contribute the constituent atoms of its transition state. (For reactions in solution this number is always taken to exclude molecular entities that form part of the medium and which are involved solely by virtue of their solvation of solutes.)

In the description of organic substitution reactions and elimination reactions the molecularity has been equated with the "number of molecules necessarily undergoing covalency change during the rate-limiting step".

See also bimolecular, order of reaction, unimolecular.

Multi-centre bond

Representation of some molecular entities solely by localized two-electron two-centre bonds appears to be unsatisfactory. Instead, multi-centre bonds have to be considered in which electron pairs occupy orbitals encompassing three or more atomic centres. Examples include the three-centre bonds in diborane, the delocalized π bonding of benzene, and bridged carbocations.

Multi-centre reaction

A synonym for pericyclic reaction. The number of "centres" is the number of atoms in the transition state that are breaking old single bonds and/or forming new bonds to atoms to which they were not previously bonded. This number does not necessarily correspond to the ring size of the transition state for the pericyclic reaction. Thus, a Diels-Alder reaction is a "four-centre reaction". This terminology has largely been superseded by the more detailed one developed for the various pericyclic reactions.

Multident

See ambident.

Narcissistic reaction

A chemical reaction that can be described as the conversion of a reactant into its mirror image, without rotation or translation of the product, so that the product enantiomer actually coincides with the image of the reactant molecule with respect to a fixed mirror plane. Examples of such reactions are cited under the entries fluxional and degenerate rearrangement.

SALEM (1971)

Neighbouring-group participation

The direct interaction of the reaction centre (usually, but not necessarily, an incipient carbenium centre) with the lone pair of electrons of an atom or with the σ- or π-electrons of a bond contained within the parent molecule but not conjugated with the reaction centre. A distinction is sometimes made between n-, σ- and π-participation.

The associated rate increase is known as "anchimeric assistance". "Synartetic acceleration" is the special case of anchimeric assistance ascribed to participation by electrons binding a substituent to a carbon atom in a β position relative to a leaving group attached to the α-carbon atom. According to the underlying model, these electrons then provide a three-centre bond (or "bridge") "fastening together" (as the word "synartetic" is intended to suggest) the α- and β-carbon atoms between which the charge is divided in the intermediate bridged carbocation formed (and in the transition state preceding its formation). The term synartetic acceleration is not now widely used.

See also intramolecular catalysis, multi-centre bond.

Nitrene

The species NH, or a substitution derivative thereof, containing electrically neutral mono-co-ordinate nitrogen with four non-bonding electrons. Two of these are paired; the other two may have parallel spins (triplet state) or antiparallel spins (singlet state). The name is the strict analogue of carbene and is preferred to a number of alternatives proposed ("imene", "imine radical", "azene", "azylene", "azacarbene", "imin", "imidogen").

See LWOWSKI (1970).

Nitrenium ion

A structure, real or hypothetical, representing a nitrogen cation that contains at least one di-co-ordinate nitrogen atom, i.e., NH_2^+ or a substitution derivative thereof. (Cf. carbenium ion.) Like nitrenes, from which nitrenium ions can be considered to be derived by addition of H^+ or R^+, nitrenium ions can exist in singlet or triplet states. (Use of the alternative name "imidonium ion" is not recommended.)

No-bond resonance

See hyperconjugation.

Normal kinetic isotope effect

See isotope effect.

Nucleofuge

A leaving group that carries away the bonding electron pair. The leaving tendency of such a group (a nucleofugic group) has been called nucleofugicity.

See also electrofuge, nucleophilic.

Nucleophile, nucleophilic

A "nucleophilic reagent" or "nucleophile" is a reagent that is preferentially attracted to a region of low electron density in a substrate. (It is in principle possible for radicals to behave in this manner.)

In a "nucleophilic substitution reaction" a nucleophilic reagent is considered to effect substitution in the other reactant and to provide both bonding electrons. For example,

$$\mathrm{EtCl} + \underset{\text{nucleophilic reagent}}{\mathrm{MeO^-}} \longrightarrow \mathrm{EtOMe} + \underset{\text{nucleofuge}}{\mathrm{Cl^-}}$$

"Nucleophilic catalysis" is catalysis by a Lewis base, involving formation of a Lewis adduct as a reaction intermediate.

See also electrophilic, nucleophilicity.

Nucleophilicity

The relative reactivity of a nucleophilic reagent. (It is also sometimes referred to as "nucleophilic power".) Qualitatively, the concept is related to Lewis basicity. However, whereas Lewis basicity is measured by relative equilibrium constants,

$$\mathrm{B{:}} + \mathrm{A} \overset{K}{\rightleftharpoons} \overset{+}{\mathrm{B}}\text{-}\overset{-}{\mathrm{A}}$$

nucleophilicity of a Lewis base is measured by relative rate constants of different nucleophilic reagents towards a common substrate, most commonly involving formation of a bond to carbon,

$$\mathrm{B{:}} + \mathrm{A\text{-}Z} \xrightarrow{k} \overset{+}{\mathrm{B}}\text{-}\mathrm{A} + \mathrm{Z{:}^-}$$

See also electrophilicity.

"Onium" ion

A cation containing a "central" atom that bears a formal positive charge and is bonded to one univalent ligand more than is normal for a neutral molecule containing that "central" atom. The suffix "-onium" occurs in the names of specific ions, e.g. NR_4^+, tetra-alkyl-ammonium; SR_3^+, trialkylsulfonium, where R = alkyl; cf., carbenium ion.

Orbital

See molecular orbital.

Orbital symmetry

The behaviour of an atomic or a localized molecular orbital under a molecular symmetry operation characterizes its orbital symmetry. For example, under a reflection in an appropriate symmetry plane, the phase of the orbital may be unchanged (symmetric), or it may change sign, i.e., the positive and negative lobes are interchanged (antisymmetric).

A principal context for the use of orbital symmetry is the discussion of chemical changes that involve "conservation of orbital symmetry". If a certain symmetry element (e.g., the reflection plane) is retained during a molecular reorganization (even involving bond rupture), an orbital must retain its symmetry type with respect to this retained symmetry feature. This principle permits the qualitative construction of correlation diagrams to show how molecular orbitals transform (and how their energies change) during idealized chemical changes (e.g., cycloaddition reactions).

An idealized single bond is a σ-bond, i.e., it has cylindrical symmetry, whereas a p-orbital or π-bond orbital has π-symmetry, i.e., it is antisymmetric with respect to reflection in a plane passing through the atomic centres with which it is associated. In ethylene, the π-bonding orbital is symmetric with respect to reflection in a plane perpendicular to and bisecting the C-C bond, whereas the π^*-antibonding orbital is antisymmetric with respect to this operation.

Considerations of orbital symmetry are frequently grossly simplified in that, for example, the π orbitals of a carbonyl group would be treated as having the same symmetry as those of ethylene, and the fact that the carbonyl group in (e.g.) camphor, unlike that in formaldehyde, has no mirror planes, would be ignored. These simplified considerations nevertheless afford the basis of one approach to the understanding of the rules which indicate whether pericyclic reactions are likely to occur under thermal or photochemical conditions.

WOODWARD and HOFFMAN (1969)

Order of reaction

If the rate of reaction (v) for any reaction can be expressed by a differential rate equation (or "rate law") of the form

$$v = k[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta} \ldots \qquad (1)$$

where [A], [B] .... are concentrations and α, β are constant exponents, and k is a constant then the reaction is said to be of order α with respect to A, of order β with respect to B ...., and of (total or overall) order $n = (\alpha + \beta + \ldots)$. The exponents $\alpha, \beta \ldots$ can be positive or negative integral or rational non-integral numbers. They are the reaction orders with respect to A,B, ... and are sometimes called "partial orders of reaction".

For a simple (elementary) reaction a partial order of reaction is the same as the stoichiometric number of the reactant concerned (s; see rate of reaction), and the overall order the same as the molecularity. For stepwise reactions there is no general connection between stoichiometric numbers and partial orders. Such reactions may have more complex rate laws, so that the *apparent* order of reaction may vary with the concentrations of the chemical species involved and with the progress of the reaction: in such cases it is not useful to speak of orders of reaction, although apparent orders of reaction may be deducible from initial rates.

The concept of order of reaction is also applicable to chemical rate processes occurring in systems for which concentration changes (and hence rates of reaction) are not themselves measurable, provided it is possible to measure a chemical flux. For example, if there is a dynamic equilibrium according to the equation $a\mathrm{A} \rightleftharpoons p\mathrm{P}$ and if a chemical flux is experimentally found (e.g., by n.m.r. line shape analysis) to be related to concentrations by the equation

$$\frac{1}{a}\,\phi_{-\mathrm{A}} = k\,[\mathrm{A}]^{\alpha}[\mathrm{L}]^{\lambda} \ldots \qquad \ldots (2)$$

then the corresponding reaction is of order α with respect to A.... and of total (or overall) order n $(= \alpha + \lambda + \ldots)$.

The proportionality factor k in equations (1) and (2) is called the (nth order) "rate constant".

The (overall) order of a reaction cannot be deduced from measurements of the rate of reaction at a single value of the concentration of a species whose concentration is constant (or effectively constant) during the course of the reaction. If the overall rate of such a reaction is, for example, given by

$$v = k\,[A]^{\alpha}\,[B]^{\beta}$$

and [B] stays constant, then the order of the reaction, as observed from the concentration change of A with time, will be α, and the rate can be expressed in the form

$$v = k_{obs}[A]^{\alpha}$$

The proportionality factor k_{obs} deduced from such an experiment is called the "observed rate constant", and it is related to the ($\alpha+\beta$)th rate constant k by the equation $k_{obs} = k[B]^{\beta}$. For the common case when $\alpha = 1$, k_{obs} is often referred to as a "pseudo-first order rate constant" (k_{ψ}).

In a stepwise reaction orders of reaction may in principle always be assigned to the elementary steps. The proportionality factor relating the chemical flux of an elementary reaction step (or of an experimentally inseparable sequence of elementary steps) to the appropriate product of concentrations of chemical species involved in that step (or stage) is called the "rate coefficient" for that step (or stage).

Oxidation

(1) The complete net removal of one or more electrons from a molecular entity.

(2) (Organic Chemistry). A transformation of an organic substrate that can notionally be dissected into steps or primitive changes consisting of the removal of one or several electrons from a substrate followed or preceded by gain or loss of solvent molecules and/or of hydrogen ions, hydroxide ions or lyate ions, or by straightforward nucleophilic substitution by solvent or by its hypothetical reversal, and/or by an (intramolecular) molecular rearrangement.

This formal definition allows the original idea of oxidation (combination with oxygen) as well as reactions closely akin to this chemical type of reaction, and generally regarded in current usage of the term in organic chemistry to be oxidations (and to be effected by "oxidizing agents"), to be related to the more restrictive first alternative definition.

Examples of oxidation reactions:

(a) Oxidation of Fe^{II} to Fe^{III}: $Fe^{2+} - e^{-} = Fe^{3+}$.

(b) Formation of an amine oxide from an amine:

$$R_3N - 2e^{-} + 2OH^{-} - H_2O = R_3NO$$

(c) Dehydrogenation of an alkane:

$$RCH_2CH_3 - 2e^{-} - 2H^{+} = RCH{=}CH_2$$

(d) Conversion of methane into dichloromethane:

$$CH_4 - 4e^{-} - 2H^{+} + 2OH^{-} = CH_2(OH)_2 \xrightarrow[\text{of hydrolysis}]{\text{reversal}} CH_2Cl_2$$

Oxidation level

This is a relative rather than an absolute term, used to compare substances that may be fairly readily interconverted and to reveal whether such conversion may be deemed to be an oxidation or reduction. Thus ethylene, ethanol, and ethyl chloride are all at the same oxidation level. Ethane is at a lower oxidation level, but acetylene, acetaldehyde, and dichloroethane are all at a (common) higher oxidation level than the first group of compounds.

The term "oxidation state" is sometimes used, but seems less satisfactory in this context.

Oxidation number

See IUPAC INORGANIC RULES, (1970), Rule O.1.

Partial rate factor

The rate of substitution at one specific site in an aromatic compound relative to the rate of substitution at *one* position in benzene. For example, the partial rate factor for *para* substitution in monosubstituted benzene, f_p^{Z} is related to the rate constants $k_{\mathrm{C_6H_5Z}}$ and $k_{\mathrm{C_6H_6}}$ for the total reaction of $\mathrm{C_6H_5Z}$ and benzene, respectively, and % *para* (the percentage of *para* substitution in the total product formed from $\mathrm{C_6H_5Z}$) by the relation

$$f_p^{\mathrm{Z}} = \frac{6k_{\mathrm{C_6H_5Z}}}{k_{\mathrm{C_6H_6}}} \quad \frac{\%\ para}{100}$$

Similarly for *meta*-substitution

$$f_m^{\mathrm{Z}} = \frac{6k_{\mathrm{C_6H_5Z}}}{2k_{\mathrm{C_6H_6}}} \quad \frac{\%\ meta}{100}$$

(The symbols p_f^{Z}, m_f^{Z} o_f^{Z}, are also in use.) The term can be extended to other substituted substrates undergoing parallel reactions at different sites with the same reagent according to the same rate law.

INGOLD (1953)

See STOCK and BROWN (1963).

See also selectivity.

Pericyclic reaction

A reaction in which concerted reorganization of bonding takes place *throughout* a cyclic array of continuously bonded atoms. It may be viewed as a reaction proceeding through a fully conjugated cyclic transition state. The term embraces a variety of concerted processes including cycloadditions, cheletropic reactions, electrocyclic and sigmatropic rearrangements, etc.

See also multi-centre reaction.

Persistent

See transient.

pH-rate profile

A plot of observed rate constant, or more usually its decadic logarithm, against pH of solution, other variables being kept constant.

Phase-transfer catalysis

The phenomenon of rate enhancement of a reaction between chemical species located in different phases (most commonly in immiscible solvents) by the addition of a small quantity of an agent (called the "phase-transfer catalyst"), commonly a surfactant, that transfers one of the reactants across the interface into the other phase so that reaction can proceed. The phase-transfer agent is not consumed in the reaction (though it may be consumed in side reactions) and functions as a catalyst.

Phenonium ion

See bridged carbocation.

Photolysis

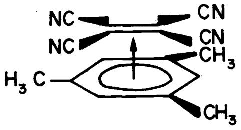
The cleavage of one or more covalent bonds in a molecular entity resulting from absorption of light, or a photochemical process in which such cleavage is an essential part. For example:

$$\mathrm{Cl_2} \xrightarrow{h\nu} 2\mathrm{Cl}\cdot$$

The term has also been used to refer to the irradiation itself ("laser photolysis", "flash photolysis"; it is recommended that this usage should not be extended beyond these established examples).

π-Adduct (pi-adduct)

An adduct formed by co-ordination, involving electron-pair donation from a π-orbital into a σ-orbital, or from a σ-orbital into a π-orbital, or from a π-orbital into a π-orbital. For example:



Such an adduct has commonly been known as a "π-complex", but, as the bonding is not necessarily weak, it is better to avoid the term complex, in accordance with the recommendation in this Glossary.

† π-Complex (pi-complex)

See π-adduct.

† Polar-aprotic (solvent)

See dipolar-aprotic.

Polar effect

An effect of a substituent group (on reaction rates, etc.) having its origin in the substituent electronegativity. (There are also other substituent effects, e.g., steric effects.)

See also field effect, inductive effect, mesomeric effect.

Polar solvent

See polarity.

Polarizabilty

The ease of distortion of the electron cloud of a chemical species by an electric field (such as that due to the proximity of a charged reagent). It is experimentally measured as the ratio of induced dipolar moment (μ_{ind}) to the field E which induces it:

$$\alpha = \mu_{ind}/E$$

In ordinary usage the term refers to the "mean polarizability", i.e., the average over three rectangular axes of the molecule. Polarizabilities in different directions (e.g. along the bond in Cl_2, called "longitudinal polarizability", and in the direction perpendicular to the bond, called "transverse polarizability") can, at least in principle, be distinguished.

See INGOLD (1953).

Polarity

When applied to a solvent, this rather ill-defined term is synonymous with ionizing power.

See also Grunwald-Winstein equation, Z-value.

Polydent

See ambident.

Potential-energy profile

A curve describing the variation of the potential energy of the system of atoms that make up the reactants and products of a reaction, as a function of one geometric co-ordinate, and corresponding to the "energetically easiest passage" from reactants to products (i.e.

along the line produced by joining the paths of steepest descent from the transition state to the reactants and to the products). For an elementary reaction the relevant geometric co-ordinate is the reaction co-ordinate; for a stepwise reaction it is the succession of reaction co-ordinates for the successive individual reaction steps. (The reaction co-ordinate is sometimes approximated by a quasi-chemical index of reaction progress, such as "degree of atom transfer" or bond order of some specified bond.)

See also potential-energy reaction surface, Gibbs energy diagram.

Potential-energy reaction surface

A diagram in which the energetically easiest progress (see potential-energy profile) of an elementary reaction (considered as the movement of a representative point of the system on the multi-dimensional potential-energy hypersurface is plotted as a function of two selected co-ordinates and on which isoenergetic contours map the potential energy of the system. The co-ordinates of the diagram characterize two variables that change during the course of the reaction. For simple reaction steps, e.g., $A - B + C \rightarrow A + B - C$, the surface can show the potential energy for all values of the A, B, C geometry providing that the ABC angle is fixed.

For more complicated reactions two rectangular co-ordinates can be selected and would typically be the bond orders of two different bonds. Such a diagram is often arranged so that reactants are located at the bottom left corner and products at the top right. If the trace of the representative point follows two adjacent edges of the diagram, the changes represented by the two co-ordinates take place in distinct succession; if the trace leaves the edges and crosses the interior of the diagram, the two changes are concerted. In many qualitative applications it is convenient (although not strictly equivalent) for the third co-ordinate to represent standard Gibbs energy rather than potential energy. (Some reservations concerning the diagrammatic use of Gibbs energies are noted under Gibbs energy diagram.)

ALBERY (1967)

MORE O'FERRALL (1970)

JENCKS (1972).

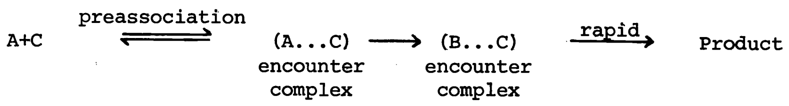
See also reaction co-ordinate.

Preassociation

A step on the reaction path of some stepwise reactions

$$A \longrightarrow B \xrightarrow{+C} \text{Product}$$

in which the molecular entity C is already present in an encounter pair or encounter complex with A during the formation of B from A, e.g.



$$A+C \overset{\text{preassociation}}{\rightleftharpoons} \underset{\substack{\text{encounter}\\ \text{complex}}}{(A\ldots C)} \longrightarrow \underset{\substack{\text{encounter}\\ \text{complex}}}{(B\ldots C)} \xrightarrow{\text{rapid}} \text{Product}$$

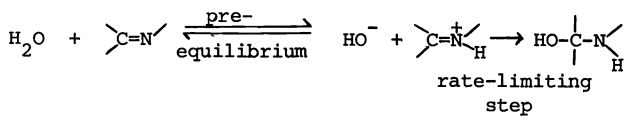
The chemical species C *may* but does not necessarily assist the formation of B from A (which may itself be a bimolecular reaction with some other reagent). If it does not, C is described as being present as a spectator, and hence such a mechanism is sometimes referred to as a "spectator mechanism".

Preassociation is important when B is too short-lived to permit B and C to come together by diffusion.

See also microscopic diffusion control.

Pre-equilibrium (or prior equilibrium)

A reversible step preceding the rate-limiting step in a stepwise reaction. For example



See also kinetic equivalence.

Pre-exponential factor

See energy of activation, entropy of activation.

Primary equilibrium isotope effect

See isotope effect.

Primary kinetic electrolyte effect

See kinetic electrolyte effect.

Primary kinetic isotope effect

See isotope effect.

Primitive change

One of the conceptually simpler molecular changes into which an elementary reaction can be notionally dissected. Such changes include bond rupture, bond formation, internal rotation, change of bond length or bond angle, bond migration, redistribution of charge, etc.

The concept of primitive changes is helpful in the detailed verbal description of elementary reactions, but a primitive change does not represent a process that is *by itself* observable as a component of an elementary reaction.

Prior equilibrium

See pre-equilibrium.

Promotion

If an acid or base is present in nearly constant concentration throughout a reaction in solution (owing to buffering or the use of a large excess) it may be found to increase the rate of that reaction and also to be consumed during the process. The acid is then not a catalyst and the phenomenon cannot be called catalysis according to the well-established meaning of these terms in chemical kinetics, although the mechanism of such a process is often most intimately related to that of a catalysed reaction. It is recommended that the more general term "promotion" be used in these and analogous cases. For example, if a Brønsted acid accelerates the hydrolysis of an ester to a carboxylic acid and an alcohol, this is properly called acid catalysis, whereas the acceleration by the same acid of the hydrolysis of an amide should be described as "promotion" by the acid: the "acid promoter" is consumed during the "acid-promoted reaction" through formation of an ammonium ion. The terms "general acid promotion" and "general base promotion" may be used as the analogues of general acid catalysis and general base catalysis. Catalysis may be taken to be a special case of promotion. (An alternative name for this phenomenon is "pseudo-catalysis".)

(The term promotion is also in use with a different meaning in other chemical contexts.)

Propagation

See chain reaction.

Protogenic (solvent)

Capable of acting as a proton donor (strongly or weakly acidic in the Brønsted sense). The term is preferred to the synonym "protic" or the more ambiguous expression "acidic" by itself.

†Protolysis

This term has been used synonymously with proton transfer reaction. Because of its misleading similarity to hydrolysis, photolysis, etc., its use is discouraged.

See also autoprotolysis.

Proton affinity

The energy released in the gas-phase reaction (real or hypothetical) between a proton and the molecular entity concerned (usually an electrically neutral molecule) to give the conjugate acid of that species.

Proton-transfer reaction

A chemical reaction, the main feature of which is the intermolecular or intramolecular transfer of a proton from one binding site to another. For example,

$$\mathrm{CH_3CO_2H} + \mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3} \rightleftharpoons \mathrm{CH_3CO_2^-} + \mathrm{CH_3}\overset{\mathrm{+OH}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3}$$

In the detailed description of rapid proton transfers between electronegative atoms it should always be specified whether the term is used to refer to the overall process (including the more-or-less encounter-controlled formation of a hydrogen-bonded complex and the separation of the products; see microscopic diffusion control) or just to the proton-transfer phase (including solvent rearrangement) by itself.

See also autoprotolysis, tautomerism.

Protophilic (solvent)

Capable of acting as proton acceptor, strongly or weakly basic (as a Brønsted base).

Prototropic rearrangement (or prototropy)

See tautomerism.

Pseudo-first order rate constant

See order of reaction.

†Pseudomolecular rearrangement

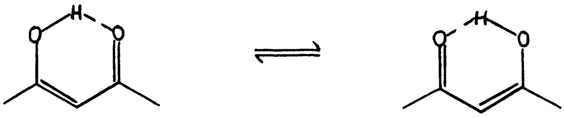
The use of this awkwardly formed term is discouraged. It is synonymous with "intermolecular rearrangement".

See molecular rearrangement.

Pseudopericyclic

A concerted transformation is pseudopericyclic if the primary changes in bonding occur within a cyclic array of atoms at one (or more) of which non-bonding and bonding atomic orbitals interchange roles.

A formal example is the enol $\rightleftharpoons$ enol prototropy of acetylacetone. Since the atomic



orbitals that interchange roles are orthogonal, such a reaction does not proceed through a fully conjugated transition state and is thus not a pericyclic reaction and therefore not governed by orbital symmetry restrictions applicable to pericyclic reactions.

ROSS, SEIDERS and LEMAL (1976).

†Pseudo-unimolecular

An ambiguous term without clear meaning.

See unimolecular and order of reaction.

Pyrolysis

Thermolysis, usually associated with exposure to a high temperature.

Quantum yield

The number of moles transformed physically (e.g.,by emission of photons) or chemically per mole of photons (Einstein) absorbed.

See CALVERT and PITTS (1966).

Radical (or free radical)

A molecular entity possessing an unpaired electron, such as $\cdot CH_3$, $\cdot SnH_3$, $\cdot Cl$ (or $Cl\cdot$). (In these formulae the dot, symbolizing the unpaired electron, should be placed so as to indicate the atom of highest spin density, if this is possible.) Paramagnetic metal ions are not normally regarded as radicals.

At least in the context of physical organic chemistry, it seems desirable to cease using the adjective "free" in the general name of this type of chemical species and molecular entity, so that the term "free radical" may in future be restricted to those radicals which do not form parts of radical pairs.

It should, however, also be noted that the name "radical", by itself, is used in the nomenclature of organic compounds (IUPAC ORGANIC RULES, 1969, Section A) to describe a hydrocarbon residue forming part of a molecule. (For example, the side chain in 3-methylpentane is a methyl radical). In physical or mechanistic organic chemistry such a part of a molecule would usually be called a substituent group or group, notwithstanding the more restrictive use of the word "group" in the nomenclature of organic compounds.

See also biradical.

Radical anion

A negatively charged radical; e.g. the benzene radical anion $C_6H_6^{\cdot-}$ or the benzophenone radical anion $Ph_2\dot{C}\text{-}O^-$.

Radical cation

A positively charged radical; e.g., the benzene radical cation $C_6H_6^{\cdot+}$.

Radical centre(s)

The atom (or group of atoms) in a polyatomic radical on which an unpaired electron is largely localized. Addition of a monovalent atom to a radical centre gives a molecule for which it is possible to write a Lewis formula in which the normal stable valencies are assigned to all atoms.

Radical combination

See colligation.

Radical disproportionation

See disproportionation.

Radical ion

A general term for either a radical anion or a radical cation.

(Unless the positions of unpaired spin and charge can be associated with specific atoms, the dot and charge indications should be placed in the order ·+ or ·− suggested by the name radical ion.)

Radical pair (or geminate pair)

The term is used to identify two radicals in close proximity in liquid solution, within a solvent cage. They may be formed simultaneously by some unimolecular process, e.g., peroxide decomposition, or they may have come together by diffusion. Whilst the radicals are together, correlation of the unpaired electron spins of the two species cannot be ignored: this correlation is responsible for CIDNP phenomena.

Radiolysis

The cleavage of one or several bonds resulting from exposure to high-energy radiation. The term has also been used to refer to the irradiation itself ("pulse radiolysis"; it is recommended that this usage should not be extended).

Rate coefficient

See order of reaction.

Rate constant

See order of reaction.

Rate law (or differential rate equation)

An expression for the rate of reaction of a particular reaction in terms of concentrations of chemical species and constant parameters (normally rate coefficients and partial orders of reaction) only. For examples of rate laws see equation (1) under "order of reaction", equations (1) to (3) under kinetic equivalence, and equation (1) under steady state.

Rate of appearance

See rate of reaction.

Rate of disappearance

See rate of reaction.

Rate of reaction

For the general elementary reaction

$$aA + bB \ldots \longrightarrow pP + qQ \ldots ,$$

occurring under constant-volume conditions, the rate of reaction (v) is defined as

$$v = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{p}\frac{d[P]}{dt} = \frac{1}{q}\frac{d[Q]}{dt} = \ldots\ldots$$

where symbols placed inside square brackets denote concentrations (conventionally expressed in units of mol dm^{-3}). The symbols R and r are also commonly used in place of v. The unit of time should always be the second.

In such a case the rate of reaction differs from the rate of increase of concentration of a product P by a constant quotient (the stoichiometric number p) and from the rate of decrease of concentration of reactant A by the quotient a. [It should be noted that the stoichiometric numbers a, b.. are always positive; this differs from the definition of the stoichiometric number ν_B in IUPAC MANUAL (1979)].

The quantity $\dot{\xi}$ $(= \frac{d\xi}{dt})$ defined by the equation

$$\dot{\xi} = \frac{1}{a}\frac{dn_A}{dt} = -\frac{1}{b}\frac{dn_B}{dt} = \frac{1}{p}\frac{dn_P}{dt} = \frac{1}{q}\frac{dn_Q}{dt} = \ldots.$$

(where n_A designates the amount of substance A, conventionally expressed in units of mol) may be called the "rate of conversion" and is appropriate for the description of reactions under conditions of varying volume. In a system of constant volume, the rate of reaction is equal to the rate of conversion per unit volume throughout the reaction.

For a stepwise reaction a unique "rate of reaction" (and "extent of reaction", ξ) will exist only if there is no accumulation of intermediate or formation of side products. It is therefore recommended that the term "rate of reaction" be used only in cases where it is experimentally established that these conditions apply. More generally, it is recommended that, instead, the terms rate of disappearance of A (i.e. $-d[A]/dt$, the rate of decrease of concentration of A) or rate of appearance of P (i.e. $d[P]/dt$, the rate of increase of concentration of product P) be used, depending on the concentration change of the particular chemical species that is actually observed. In some cases reference to the chemical flux observed may be more appropriate.

N.B.: This definition differs from the unconventional terminology proposed by IUPAC Commission I.1 [see IUPAC MANUAL (1979)],but conforms to CODATA recommendations [see CODATA (1974)].

Rate-controlling step

See rate-limiting step.

Rate-determining step

If in a stepwise reaction the rate of formation of product is determined *solely* by the rate coefficient of the *first* step and the concentrations of the reactants (without in any way involving rate or equilibrium constants of other steps), then the first step of the reaction may be described as the rate-determining step.

The term "rate-determining step" is not synonymous with rate-limiting step: all rate-determining steps are also rate-limiting, but the converse is not true.

Rate-limiting step (or rate-controlling step)

If for a stepwise reaction

$$\begin{array}{ccccc} A + B \xrightleftharpoons{K_1} C + D & \xrightleftharpoons{K_2} & \ldots \xrightleftharpoons[k_{-g}]{k_g} G & \xrightleftharpoons[+\,X]{k_j} & P \xrightleftharpoons{k_l} Q \ldots. \\ \text{step } 1 & \text{step } 2 & \text{step } g & \text{step } j & \text{step } l \end{array}$$

which corresponds to a sequence of elementary reactions in a homogeneous system, the rate of reaction (v) can be expressed by:

$$v = F\,([A],[B],[C],[D], \ldots.., K_1,K_2,\ldots.) \times k_j\ [X]$$

where F is a function only of the concentrations and of the equilibrium constants K_i for the pre-equilibria that precede the step j, then step j is called the rate-limiting step.

In such a sequence, step j is the earliest step for which the forward chemical flux (divided, if appropriate, by the corresponding stoichiometric number, is practically equal to the rate of formation of the final reaction product (similarly divided), if the overall process is irreversible. (If the overall process is reversible, then the rate-limiting step is the step for which the forward chemical flux is least in excess of the rate of reaction). If $\Sigma\phi_G > \Sigma\phi_P$ and $\phi_{-g} \sim \phi_j$, then neither step g nor step j is separately rate-limiting. In such cases the two steps have been described as "jointly rate-limiting").

The term "rate-limiting" does not imply that such a step imposes an upper limit on the rate of reaction (as under conditions of saturation in Michaelis-Menten kinetics). For this reason, the synonym "rate-controlling step", although not widely used at present, is preferable where there is a possibility of such confusion.

"Rate-limiting step" is not synonymous with rate-determining step.

For heterogeneous systems the above analysis requires modification to allow for the role of mass transfer.

See also macroscopic diffusion control, microscopic diffusion control.

Reaction co-ordinate

A geometric parameter that changes during the conversion of one (or more) reactant molecular entities to one (or more) product molecular entities and whose value can be taken as a measure of the progress of an elementary reaction. (For example, a bond length or bond angle or a combination of bond lengths and/or bond angles; it is sometimes approximated by a non-geometric parameter, such as the bond order of some specified bond.)

In the formalism of "transition state theory", the reaction co-ordinate is that co-ordinate in a set of curvilinear co-ordinates obtained from the conventional ones for the reactants which, for each reaction step, leads smoothly from the configuration of the reactants through that of the transition state to the configuration of the products. The reaction co-ordinate is typically chosen to parallel the path of minimum potential energy from reactants to products.

The term has also been used interchangeably with the term transition co-ordinate, applicable to the co-ordinate in the immediate vicinity of the potential energy maximum. Being more specific, the name transition co-ordinate is to be preferred in that context.

See MARCUS (1966).

See also potential-energy profile; potential-energy reaction surface.

Reaction intermediate

A transient chemical species, with a lifetime appreciably longer than a molecular vibration (corresponding to a local potential energy minimum of depth greater than RT), that is formed (directly or indirectly) from the reactants and reacts further to give (either directly or indirectly) the products of a chemical reaction.

See also reaction step, elementary reaction, stepwise reaction.

Reaction mechanism

See mechanism.

Reaction path

(1) A synonym for mechanism.

(2) A trajectory on the potential energy surface.

Reaction stage

A set of one or more (possibly experimentally not separable) reaction steps leading to and/or from a detectable or presumed reaction intermediate.

Reaction step

An elementary reaction, constituting one of the stages of a stepwise reaction, in which a reaction intermediate (or, for the first step, the reactants) is converted to the next reaction intermediate (or, for the last step, the products) in the sequence of intermediates between reactants and products.

See also rate-limiting step, reaction stage.

Reactive, reactivity

As applied to a chemical species, the terms express a kinetic property. A species is said to be more reactive or to have a higher reactivity in some given context than some other (reference) species if it has a larger rate constant for a specified elementary reaction *with the same reaction partner*. The term has meaning only by reference to some explicitly stated or implicitly assumed standard.

See also stable, unreactive, unstable.

Reactivity index

Any numerical index derived from quantum - mechanical model calculations that permits the prediction of relative reactivities of different molecular sites. Many indices are in use, based on a variety of theories and relating to various types of reaction. The more successful applications have been to the substitution reactions of conjugated systems, where relative reactivities are determined largely by changes of π-electron energy.

Rearrangement

See molecular rearrangement, degenerate rearrangement.

Rearrangement stage

The elementary reaction or reaction stage (of a molecular rearrangement) in which there is both making and breaking of bonds between atoms common to a reactant and a reaction product. If the rearrangement stage consists of a single elementary reaction, this is a "rearrangement step".

Reduction

(1) The complete net transfer of one or more electrons to a molecular entity.

(2) (Organic chemistry). A transformation of an organic substrate that can notionally be dissected into primitive changes consisting of the transfer of one or several electrons to a substrate, followed or preceded by gain or loss of solvent molecules and/or of hydrogen ion, hydroxide ions or lyate ions, or by straightforward nucleophilic substitution by solvent or by its hypothetical reversal, and/or by an (intramolecular) molecular rearrangement.

(The reasons for this formal definition are analogous to those given under the definition of oxidation.)

See also electronation.

Regioselective, regioselectivity

A regioselective reaction is one in which a chemical change occurs preferentially at one of several possible sites in a molecule (usually involving at each site a functional group of the same structural type). Reactions are termed completely (100%) regioselective if the discrimination is complete, or partially (x%) regioselective if the product of reaction at one site predominates over the products of reaction at other sites. The descrimination may also semi-quantitatively be referred to as high or low regioselectivity.

(Originally, the term was restricted to addition reactions of unsymmetrical reagents to unsymmetrical alkenes.)

Resonance

As used in chemistry, the term refers to be representation of the electronic structure of a molecular system in terms of contributing structures, and often symbolized by a double-headed arrow between contributing structures. Resonance among contributing structures means that the wave function is approximately represented by "mixing" the wave functions of contributing structures. The concept is the basis of the quantum-mechanical valence bond method. The resulting stabilization is linked to the quantum-mechanical concept of "resonance energy".

See ATKINS (1974).

See also delocalization, mesomerism.

Resonance effect

See mesomeric effect.

Resonance energy.

See resonance.

†Retroaddition

See cycloreversion.

†Retrocycloaddition

See cycloreversion.

Retro-ene reaction

See ene reaction.

Reverse micelle (or reversed micelle)

See inverted micelle.

ρ-value (rho-value)

A measure of the susceptibility to the influence of substituent groups on the rate constant or equilibrium constant of a particular organic reaction involving a family of related substrates. Defined by Hammett for the effect of ring substituents in *meta-* and *para-* positions on aromatic side-chain reactions by the empirical "ρσ - equation" of the general form:

$$\lg \frac{k_X}{k_H} = \rho\sigma_X$$

in which σ_X is a constant characteristic of the substituent X and of its position in the reactant molecule.

More generally, ρ-values (modified with appropriate subscripts and superscripts) are used to designate the susceptibility of reaction series for families of various organic compounds, and not only for aromatic series, to any substituent effects, as given by the use of any modified set of σ-constants in an empirical ρσ-correlation.

A more positive value of ρ qualitatively indicates that a specific region in the transition state (or in the organic products, in the case of an equilibrium constant) of a particular reaction has a greater tendency to concentrate a negative charge (or smaller tendency to concentrate a positive charge) at the expense of the substituent groups, than is the case for the reference reaction.

See also Taft equation.

ρσ-Equation (rho-sigma equation)

See rho-value.

†Salt effect

See kinetic electrolyte effect.

Saytzeff rule

"Dehydrohalogenation of secondary- and tertiary-alkyl halides proceeds by the preferential removal of the β-hydrogen from the carbon that has the smallest number of hydrogens." Originally formulated by A. Saytzeff to generalize the orientation in β-elimination reactions of alkyl halides, this rule has been extended and modified, as follows: "When two or more alkenes can be produced in an elimination reaction, the thermodynamically most stable olefin will predominate." The thermodynamically most stable olefin is usually also the most highly substituted olefin. Exceptions to the Saytzeff rule are exemplified by the Hofmann rule.

SAYTZEFF (1875).

Scavenger

A substance that reacts with (or otherwise removes) a trace component (as in the scavenging of trace metal ions) or traps a reactive reaction intermediate.

See also inhibition.

Secondary equilibrium isotope effect

See isotope effect.

Secondary kinetic electrolyte effect

See kinetic electrolyte effect.

Secondary kinetic isotope effect

See isotope effect.

Selectivity

The discrimination shown by a reagent in competitive attack on two or more substrates or on two or more positions in the same substrate. It is quantitatively expressed by ratios of rate constants of the competing reactions, or by the decadic logarithms of such ratios.

Selectivity factor

A quantitative representation of selectivity in aromatic substitution reactions (usually electrophilic, for mono-substituted benzene derivatives). If the partial rate factor, f, expresses the reactivity of a specified position in the aromatic compound PhX relative to that of a single position in benzene, then the selectivity factor S_f expressing discrimination between *p*- and *m*-positions in PhX) is defined as lg (f_p^{X}/f_m^{X}).

STOCK and BROWN (1963).

σ-adduct (sigma-adduct)

The product formed by the addition of an electrophilic or nucleophilic entering group or of a radical to a ring carbon atom of an aromatic species such that a new σ-bond is formed and the original conjugation is disrupted. (This has generally been called a "σ-complex", but adduct is more appropriate than complex according to the definitions given.) The term may also be used for analogous adducts to unsaturated (and conjugated) systems in general.

See also Meisenheimer adduct.

σ-constant (sigma-constant)

Hammett's substituent constant, defined as lg (K_a/K_a^o), where K_a is the ionization constant of a *meta-* or *para-* substituted benzoic acid in water at 25°C, and K_a^o that of benzoic acid itself.

The term is also in use as a collective description for related substituent constants, applicable to restricted ranges of observations, of which σ^+, σ^- and σ^o are typical. Such substituent constants are designated by the letter σ with various subscripts and superscripts. They are defined in the references cited below.

In a qualitative sense, a large positive σ-value implies high electron-withdrawing power, etc.

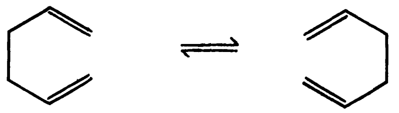
See also ρ-value, Taft equation.

See CHAPMAN and SHORTER (1972); JOHNSON (1973); SHORTER (1973).

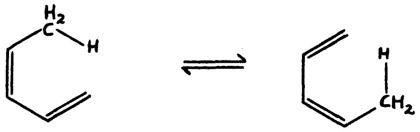
Sigmatropic

A "sigmatropic" reaction is an intramolecular pericyclic rearrangement that involves the breaking of an existing σ-bond and the creation of a new σ-bond between previously unconnected atoms. There is normally a concurrent relocation of π-bonds in the molecule concerned, but the total number of π- and σ-bonds will not change.

The transition state of a sigmatropic process may be visualized as an association of two fragments connected at their termini by two partial σ-bonds, one being broken and the other being formed. Considering only atoms within the cyclic array undergoing pericyclic reorganization, if the numbers of these in the two fragments are designated i and j, then the rearrangement is said to be a sigmatropic change of order $[i,j]$. Thus the rearrangement (a) is of order [3,3], whilst reaction (b) is a [1,5] sigmatropic shift of hydrogen.

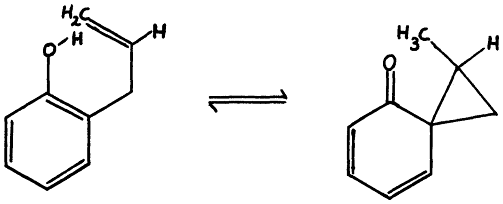


(a)



(b)

The prefix "homo" (meaning one extra participating atom - cf. "homoaromatic") has frequently been applied to sigmatropic rearrangements, but is misleading. The apparent homo [1,5] sigmatropic rearrangement (c) does not fit the above definition. This reaction is better classified as an intramolecular ene-reaction.



(c)

Silylene

(1) An uncharged di-co-ordinate silicon compound in which silicon is linked to two adjacent groups by covalent bonds and possesses two non-bonding electrons, i.e., the silicon analogue of carbene.

(2) The silanediyl group ($H_2Si<$), analogous to the methylene group ($H_2C<$).

Soft acid

Qualitatively, a Lewis acid with an acceptor centre of high polarizability which preferentially associates with soft bases rather than with hard bases. For example, a soft acid prefers an S- (or P-) base to its O- (or N-) analogue.

See also class (a) metal ion, hard acid.

Soft base

Qualitatively, a Lewis base with a donor centre (e.g. an S atom) of high polarizability and which may possess vacant orbitals of low energy. Soft bases associate preferentially with soft acids rather than with hard acids.

See also class (b) metal ion, hard base.

Solvation

Any stabilizing interaction of a solute (or solute moiety) and the solvent or a similar interaction with solvent of groups of an insoluble material (e.g., the ionic groups of an ion-exchange resin). Examples of such interactions are hydrogen-bonding, electrostatic and van der Waals forces.

See also cybotactic region.

Solvent isotope effect

See isotope effect.

Solvent polarity

See Grunwald-Winstein equation, ionizing power, Z-value.

Solvent-separated ion pair

See ion pair.

Solvent-shared ion pair

See ion pair.

Solvolysis

Generally, reaction with a solvent, or with a lyonium ion or lyate ion, involving the rupture of one or more bonds in the reacting solute. More specifically the term is used for substitution, elimination and fragmentation reactions in which a solvent species is the nucleophile, ("alcoholysis" if the solvent is an alcohol, etc.).

SOMO

A singly occupied molecular orbital (usually the half-filled HOMO of a radical).

See also frontier orbitals.

Species

See chemical species.

Specific catalysis

The acceleration of a reaction by a specific catalyst only, rather than by a family of related substances. The term is most commonly used in connection with specific hydrogen-ion or hydroxide-ion catalysis.

See also general acid catalysis, general base catalysis, promotion.

Spectator mechanism

See preassociation.

Spin adduct

See spin trapping.

Spin counting

See spin trapping.

Spin trapping

In certain solution reactions a transient radical will interact with a diamagnetic reagent to form a more persistent radical. The product radical accumulates to a concentration where detection and, frequently, identification are possible by e.s.r. spectroscopy. The key reaction is usually one of addition; the diamagnetic reagent is said to be a "spin trap", and the persistent product radical is then the "spin adduct". The procedure is referred to as "spin trapping", and is used for monitoring reactions involving the intermediacy of reactive radicals at concentrations too low for direct observation. Typical spin traps are C-nitroso-compounds and nitrones, to which reactive radicals will rapidly add to form nitroxide radicals. A quantitative development, in which essentially all reactive radicals generated in a particular system are intercepted, has been referred to as "spin counting". Spin trapping has also been adapted to the interception of radicals generated in both gaseous and solid phases. In these cases the spin adduct is in practice transferred to a liquid solution for observation in order to facilitate the interpretation of the e.s.r. spectra of the radicals obtained.

Stable

As applied to chemical species, the term expresses a thermodynamic property, which is quantitatively measured by relative molar standard Gibbs energies. A chemical species A is more stable than its isomer B if $\Delta G^{\ominus} > 0$ for the (real or hypothetical) reaction A → B, under stated conditions. If for two reactions

$$P \longrightarrow X + Y \qquad (\Delta G_1^{\ominus})$$
$$Q \longrightarrow X + Z \qquad (\Delta G_2^{\ominus})$$

$\Delta G_1^{\ominus} > \Delta G_2^{\ominus}$, P is more stable relative to the product Y than Q is relative to Z. Both in qualitative and quantitative usage the term stable is therefore always used by reference to some explicitly stated or implicitly assumed standard.

The term should not be used as a synonym for unreactive.

See also unstable, inert.

Stationary state

See steady state.

Steady state (or stationary state)

(1) A reactive reaction intermediate (X) reaches a steady state in a reaction sequence when the processes leading to its formation and those resulting in its removal are nearly in balance (i.e., the chemical flux into X is nearly equal to the chemical flux out of X), so that the rate of its change of concentration is negligible compared with the rate of change of concentration of other species involved. For example, for a sequence of reactions

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{X}$$

$$\mathrm{X} + \mathrm{C} \xrightarrow{k_2} \mathrm{D}$$

involving one low-concentration reactive intermediate X, the Bodenstein steady-state approximation $\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{d}t} = 0$ leads to the expression

$$\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = \frac{k_1 k_2 [\mathrm{A}][\mathrm{C}]}{k_{-1} + k_2[\mathrm{C}]} \qquad \text{.... (1)}$$

N.B.: The term is used with a more rigorous meaning by mathematicians.

(2) In a stirred flow reactor a steady state implies a regime such that all concentrations are independent of time.

Stepwise reaction

A reaction with at least one reaction intermediate, which is therefore composed of at least two consecutive elementary reactions.

Stereochemical

Relating to isomerism due to differences in the spatial arrangement of bonds without any differences in connectivity or bond multiplicity between the isomers.

Stereoelectronic

Pertaining to the dependence of the electronic state (and, especially, its energy) of a molecular entity or transition state on relative nuclear geometry. The electronic ground state is usually considered, but the term can apply to excited states as well.

Stereoelectronic control

Control of the stereochemical course of a reaction by stereoelectronic factors. The term is usually applied in the framework of an orbital approximation. The variations of molecular orbital energies with relative nuclear geometry (along a reaction co-ordinate) are then seen as consequences of variations in basis-orbital overlaps.

Stereoselective, stereoselectivity

A stereoselective reaction is one in which a chemical change occurs to form preferentially one of two or more alternative products that differ only in their stereochemistry. Reactions are termed completely (100%) stereoselective if the discrimination is complete, or partially (x%) stereoselective if one product predominates. The discrimination may also semi-quantitatively be referred to as high or low stereoselectivity.

See ELIEL (1962).

[For the meaning of the term "stereoselective polymerization" see IUPAC POLYMERS (1974).]

See also stereospecific.

Stereospecific

(1) A reaction is termed stereospecific if starting materials differing only in their stereoisomerism are thereby converted into stereoisomerically different products. According to this definition, a stereospecific process is necessarily stereoselective but not all stereoselective processes are stereospecific.

† (2) The term has also been applied to describe a reaction of high ($>$ 98%) stereoselectivity, but this usage is unnecessary and is discouraged.

See ELIEL (1962).

[For the meaning of the term "stereospecific polymerization" see IUPAC POLYMERS (1974).]

Steric effect

An increase (or decrease) in a rate constant (or in an equilibrium constant), relative to a model compound, as a result of a difference in strain between, on the one hand, reactants and, on the other hand, a transition state ("steric acceleration", "steric retardation") or reaction products. (The adjective "steric" is not to be confused with stereochemical.)

Stoichiometric number

See rate of reaction.

Stopped flow

A technique for following the kinetics of reactions in solution (usually in the millisecond time range and slower) in which two reactant solutions are rapidly mixed by being forced through a mixing chamber and the flow of the mixed solution along a uniform tube is then suddenly arrested. At a fixed position along the tube the solution is monitored (as a function of time following the stoppage of flow) by some method with a rapid response (e.g. photoelectric photometry).

Strain

Strain is present in a chemical species or transition state if the bond lengths, bond angles, or dihedral angles ("torsional strain") are different from their typical values in related molecules, or if the distances between non-bonded atoms are shorter than the sum of the van der Waals radii of the atoms.

It is quantitatively defined as the enthalpy of a structure relative to a strainless structure (real or hypothetical) made up from the same atoms with the same types of bonding. (The enthalpy of formation of cyclopropane is 53.6 kJ mol^{-1}, whereas the enthalpy of formation based on three "normal" methylene groups, from acyclic models is -61.9 kJ mol^{-1}. On this basis cyclopropane is destabilized by 115.5 kJ mol^{-1} of strain energy.

Subjacent orbital

The next-to-highest occupied molecular orbital ("NHOMO"). Subjacent orbitals are sometimes found to play an important role in the interpretation of molecular interactions according to the frontier orbital approach.

See BERSON (1972).

Substituent electronegativity

The power of a substituent group to attract electrons to itself in comparison with a reference substituent, such as -H or $-CH_3$.

See also electronegativity.

Substituent group

An atom or continuous group of bonded atoms that can be considered to have replaced a hydrogen atom (or two hydrogen atoms in the special case of divalent groups) in the molecular entity of a real or hypothetical parent chemical species.

Substitution reaction

An elementary or stepwise reaction in which one atom or group in a molecular entity is replaced by another atom or group. For example,

$$CH_3Cl + OH^- \longrightarrow CH_3OH + Cl^-$$

Substrate

A compound of particular interest, the reaction of which with some other chemical reagent is under observation (e.g., a compound that is transformed under the influence of a catalyst). The term should be used with care. Either the context or a specific statement should always make it clear which chemical species in a reaction is regarded as the substrate.

Superacid

A medium having a high acidity, generally greater than that of 100% sulphuric acid. The common superacids are made by dissolving a powerful Lewis acid (e.g., SbF_5) in a suitable Brønsted acid, such as HF or HSO_3F. (An equimolar mixture of HSO_3F and SbF_5 is known by the trade name "magic acid").

Suprafacial

See antarafacial.

Synartetic acceleration

See neighbouring-group participation.

Synchronous

A concerted process in which the primitive changes concerned (generally bond rupture and bond formation) have progressed to the same (or comparable) extent at the transition state is said to be synchronous. The term figuratively implies a more or less synchronized progress of the changes. However, the progress of a bonding change (or other primitive change) has not quantitatively been defined in terms of a single parameter applicable to different bonds or different bonding changes. (Changes in fractional bond order would, in principle, provide such an index, if it were possible to define them in a physically unambiguous fashion.) The concept is therefore in general only qualitatively descriptive and does not admit an exact definition except in cases of concerted processes involving changes in two identical bonds (i.e., between the same and/or structurally equivalent atoms) and then only if they have symmetrical transition states.

Thus the bimolecular isotope exchange

$$I^- + RI^* \longrightarrow I^{-*} + RI$$

may be an exactly synchronous process, and an addition reaction $R_2C{=}CR_2 + X_2 \longrightarrow$ *may* also conceivably be one, for instance if it involves a transition state in which the two C-X

bond lengths, and the two angles XCC are equal. (N.B.: The foregoing examples are not intended to convey a view as to the actual mechanisms of these reactions, which may or may not involve concerted and/or synchronous processes.)

The view is strongly held by some active workers in the field that the use of this term can be seriously misleading and is best avoided.

T-jump

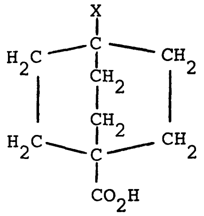
A technique for following the kinetics of rapid reactions based on the observation of attainment of equilibrium of a system following a rapid temperature rise.

Taft equation

A $\rho\sigma$-equation with modified parameters ρ_I, σ_I, used in correlations of polar effects in reactions of aliphatic compounds,

$$\mathrm{lg}\ (k_X/k_H) = \rho_I\ \sigma_I$$

where $\sigma_I = \mathrm{lg}(K_X/K_H)$, referring to acid dissociation constants of the acids



or $\sigma_I = 0.262\ \mathrm{lg}(K_X/K_H)$, referring to substituted acetic acids XCH_2COOH.

TAFT (1952,1953)

See also ρ-value, σ-constant.

†Tautomeric mechanism (obsolete)

See electromeric effect.

Tautomerism

A (generally rapid) reversible and usually intermolecular isomerization involving heterolysis and subsequent recombination of the fragments. This process can occur either with accompanying bond migration of a double bond or with ring opening (in one direction of the isomerization) and ring closure (in the reverse direction). The most familiar example of tautomerism is the case where the transferred group concerned is a proton, when one speaks of "prototropy" (or "prototropic rearrangement"). If a different cationic or an anionic group migrates, the terms "cationotropy" (or "cationotropic rearrangement") and "anionotropy", (or "aniontropic rearrangement") respectively, have been used.

See also molecular rearrangement, valence tautomerism.

Telesubstitution

A substitution reaction in which the entering group takes up a position more than one atom away from the atom to which the leaving group was attached.

See also cine-substitution.

Telomerization

A telomer is a polymer having uniform end groups of the form $X_1.......X_2$. Telomerization may be thought of as a chain transfer in which some reagent $X_1\text{—}X_2$ becomes a major feature of the polymerization process. An example would be polymerization of styrene in the presence of CCl_4 to form $CCl_3[CH_2\text{-}CH(C_6H_5)]_nCl$, with n greater than 1 and often less than about 10. A simple addition reaction, such as $CBrCl_3 + CH_2\text{=}CHR$ to give CCl_3CH_2CHBrR, is not usually considered as telomerization.

Termination

The steps in a chain reaction in which reactive reaction intermediates are destroyed or rendered inactive, thus ending the chain.

Tetrahedral intermediate

A reaction intermediate in which an initially double-bonded carbon atom (typically a carbonyl carbon atom) has been transformed from a trigonal to a tetrahedral arrangement of bonds. (For example, aldol in the condensation reaction of acetaldehyde, but most tetrahedral intermediates have a more fleeting existence.)

Thermodynamic control (of product composition)

The term characterizes conditions that lead to reaction products in a proportion determined only by the equilibrium constants for their interconversion and/or for the interconversion of reaction intermediates formed in or after the rate-limiting step. (Some workers prefer to describe this phenomenon as "equilibrium control"). (Cf. kinetic control.)

Thermolysis

The uncatalysed cleavage of one or more covalent bonds resulting from exposure of the compound to a raised temperature, or a process in which such cleavage is an essential part.

See also pyrolysis.

Tight ion pair

See ion pair.

Transient (chemical species)

Relating to a short-lived reaction intermediate. It can be defined only in relation to a time scale fixed by the experimental conditions and the limitations of the technique employed in the detection of the intermediate. The term is a relative one: intermediates having a relatively longer mean-life are described as "persistent".

Transition co-ordinate

The normal co-ordinate (of a transition state) corresponding to a vibration with an imaginary frequency. The energy maximum along this co-ordinate occurs at the transition state, and motion along it leads towards products.

See also reaction co-ordinate.

Transition state

In theories describing elementary reactions it is usually assumed that there is a transition state of more positive molar Gibbs energy between the reactants and the products through which an assembly of atoms must pass on going from reactants to products in either direction. In the formalism of "transition state theory" the transition state of an elementary reaction is that set of states (each characterized by its own geometry and energy) such that an assembly of atoms, when randomly placed there, would have an equal probability of forming the reactants or of forming the products of that elementary reaction. This set of states is characterized by $q_{\ddagger}$, the partition function for the transition state. When formed from "reactants", such an assembly passing through the transition state is assumed to continue only to the products, whereas one formed from "products" is assumed to proceed only to the "reactants".

In a more qualitative fashion a transition state is sometimes described as an "early transition state" or as a "late transition state". The clearest application of the use of these terms is linked to the Hammond principle. The energy of an early transition state of an elementary reaction is close to that of the initial state, and only a small reorganization of molecular structure occurs between these two states. A late transition state, having an energy close to that of the final state, will require little reorganization of molecular structure between the transition state and the final state.

It may be noted that calculations of reaction rates by the transition state method and based on calculated potential energy surfaces refer to the potential energy maximum at the saddle point, as this is the only point for which the requisite separability of transition state co-ordinates may be assumed. The ratio of the number of assemblies of atoms that pass through to the products to the number of those that reach the saddle point from the reactants can be less than unity, and this fraction is the transmission coefficient, κ.

See also activated complex, Gibbs energy of activation, potential-energy profile.

Transmission coefficient

See transition state.

Transport control

See microscopic diffusion control.

Trapping

The interception of a reactive molecule or reactive reaction intermediate so that it is removed from the system or converted to a more stable form for study or identification.

See also scavenger.

Unimolecular

Having a molecularity of unity.

The term describes an elementary reaction of a single reactant. Such a reaction involves a transition state composed of atoms originating in a single reactant molecule. Elementary reactions in solution are considered as unimolecular if the solvent is not covalently incorporated, wholly or in part, in the products.

When applied to a mechanism, the term implies that the rate-limiting step is a unimolecular elementary reaction.

See also bimolecular.

Unreactive

The opposite of reactive, i.e., the chemical species concerned reacts more slowly with the same reaction partner in a given context than does some assumed standard. The term should not be used in place of stable, since a relatively more stable species may nevertheless be more reactive than some reference species towards a given reaction partner.

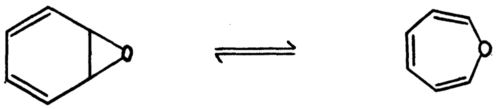
Unstable

The opposite of stable, i.e. the chemical species concerned has a higher molar Gibbs energy than some assumed standard. The term should not be used in place of reactive or transient, although more reactive or transient species are frequently also more unstable.

(Very unstable chemical species tend to undergo exothermic unimolecular decompositions. Variations in the structure of related chemical species of this kind generally affect the energy of the transition states for these decompositions less than they affect the stability of the decomposing chemical species. *In this context*, low stability may therefore parallel a relatively high rate of unimolecular decomposition.)

Valence tautomerism

The term describes simple reversible and generally rapid isomerizations or degenerate rearrangements involving the formation and rupture of single and/or double bonds, without migration of atoms or groups, e.g.



See also fluxional.

van der Waals forces

The attractive forces between molecular entities other than those due to bond formation or to the electrostatic interaction of ions or of ionic groups with one another or with neutral molecules.

Vinyl cation (or vinylic cation)

The species $CH_2=\overset{+}{C}H$ or a substitution derivative thereof.

See also carbynium ion.

Volume of activation, $\Delta V^{\ddagger}$

A quantity derived from the pressure dependence of the "rate constant" of a reaction (mainly used for reactions in solution), defined by the equation

$$\Delta V^{\ddagger} = - RT \left(\frac{\partial \ln k}{\partial p} \right)_T$$

providing that the rate constants of all reactions (except first-order reactions) are expressed in pressure-independent concentration units, such as mol dm^{-3} at a fixed temperature and pressure.

The volume of activation is interpreted, according to transition-state theory as the difference between the partial molar volume of the transition state ($V^{\ddagger}$) and the sum of the partial molar volumes of the reactants at the same temperature and pressure, i.e.,

$$\Delta V^{\ddagger} = V^{\ddagger} - \sum_{R} r \ V_R$$

where r is the stoichiometric number of the reactant R in the reaction (see order of reaction) and V_R its partial molar volume.

Ylide

A chemical species produced (actually or notionally) by loss of a proton from an atom directly attached to the central heteroatom of an "onium" ion, e.g.

$$Ph_3\overset{+}{P}\text{-CHRR'} \xrightarrow{-H^+} (Ph_3\overset{+}{P}\text{-}\overset{-}{C}\text{RR'} \longleftrightarrow Ph_3P\text{=CRR'})$$

ylide

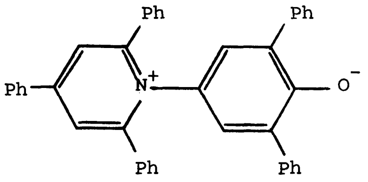
Z-value

An index of the ionizing power of a solvent based on the frequency of the longest wavelength electronic absorption maximum of 1-ethyl-4-methoxycarbonyl pyridinium iodide in the solvent. The Z-value is given by

$$Z=(2.859 \times 10^4/\lambda) \text{ nm}^{-1} \text{ kcal mol}^{-1}$$

where λ is expressed in nanometres.

A similar scale is the E_T scale derived in an exactly analogous way from the visible spectrum of



E_T is given by

$$E_T = (1.1962 \times 10^5/\lambda) \text{ nm}^{-1} \text{ kJ mol}^{-1}$$

KOSOWER (1958)

DIMROTH, REICHARDT, SIEPMANN and BOHLMANN (1963).

Zaitsev rule

See Saytzeff rule.

REFERENCES

(Reports and Rules drafted by other IUPAC Commissions are indicated by an asterisk.)

ABRAMOVITCH, R. A. (1973.
"Organic Reactive Intermediates" (S. P. McManus, ed.), Academic Press, New York.

ALBERY, W. J. (1967)
Prog. Reaction Kinetics, 4, 353.

ATKINS, P. W. (1974)
"Quanta: a handbook of concepts", Clarendon Press, Oxford.

BENSON, S. W. (1976)
"Thermochemical Kinetics", Second Edition, Wiley-Interscience, New York.

BENTLEY, T. W. and SCHLEYER, P. von R. (1977).
Adv. Phys. Org. Chem., 14, 1.

BERSON, J. A. (1972)
Accounts Chem. Res., 5, 406.

BREDT, J., THOUET, H. and SCHMIDT, J. (1924).
Ann., 437, 1.

CALVERT, J. G. and PITTS, J. N. (1966)
"Photochemistry", John Wiley & Sons, New York.

CHAPMAN, N. B. and SHORTER, J. (eds.) (1972)
"Advances in Linear Free Energy Relationships", Plenum.

CODATA (1974)
Codata Bulletin No. 13, Dec. 1974, p. 4.

DEWAR, M. J. S. (1971)
Angew. Chem. Internat. Edn., 10, 761.

DIMROTH, K., REICHARDT, C., SIEPMANN, T. and BOHLMANN, F. (1963).
Ann. Chem., 661, 1.

ELIEL, E. L. (1962)
"Stereochemistry of Carbon Compounds", McGraw Hill, New York.

FAINBERG, A. H. and WINSTEIN, S. (1956)
J. Amer. Chem. Soc., 78, 2770.

FAWCETT, F. S. (1950)
Chem. Rev., 47, 219.

GOMPPER, R. (1964)
Angew. Chem. Internat. Edn., 3, 560.

GROB, C. A. (1969)
Angew. Chem. Internat. Edn., 8, 535.

GRUNWALD, E. and WINSTEIN, S. (1948)
J. Amer. Chem. Soc., 70, 846.

HAMMOND, G. S. (1955)
J. Amer. Chem. Soc., 77, 334.

HEILBRONNER, E. (1964)
Tetrahedron Lett., 1923.

HINE, J. (1977)
*Adv. Phys. Org. Chem., 15,*1.

HOFMANN, A. W. (1851)
Ann., 78, 253; *79,* 11.

INGOLD, C. K. (1953)
"Structure and Mechanism in Organic Chemistry", Cornell University Press, New York.

*IUPAC INORGANIC RULES (1970)
IUPAC: Nomenclature of Inorganic Chemistry. Definitive Rules 1970: Butterworths, London.

*IUPAC MANUAL (1979)
IUPAC: Division of Physical Chemistry: Commission on Symbols, Terminology and Units. Manual of Symbols and terminology for physico-chemical quantities and units. *Pure Appl. Chem.*, *51*, 1.

*IUPAC MANUAL APPENDIX II (1972)
IUPAC: Division of Physical Chemistry. Manual of symbols and terminology for physico-chemical quantities and units. Appendix II. *Pure Appl. Chem.*, *31*, 577.

*IUPAC ORGANIC RULES (1969)
IUPAC: Nomenclature of organic chemistry: definitive rules, 1969. Sections A, B and C, Butterworths, London.

*IUPAC ORGANIC STEREOCHEMISTRY RULES (1974)
IUPAC: Organic Chemistry Division: Commission on nomenclature of organic chemistry III.1. Rules for the nomenclature of organic chemistry. Section E. Stereochemistry, 1974, Butterworths, London.

*IUPAC POLYMERS (1974)
IUPAC: Macromolecular Division. Commission on macromolecular nomenclature. Basic definitions of terms relating to polymers, 1974.

JENCKS, W. P. (1972)
Chem. Rev., *72*, 705.

JOHNSON, C. D. (1973)
"The Hammett Equation", Cambridge University Press.

KIRKWOOD, J. G. and WESTHEIMER, F. H. (1938)
J. Chem. Phys., *6*, 506, 513.

KOHNSTAM, G. (1967)
Adv. Phys. Org. Chem., *5*, 121.

KOSOWER, E. M. (1958)
J. Amer. Chem. Soc., *80*, 3253.

LEFFLER, J. E. (1953)
Science, *117*, 340.

LEFFLER, J. E. (1955)
J. Org. Chem., *20*, 1202.

LWOWSKI, W. (1970)
"Nitrenes", Interscience Inc., New York.

MARCUS, R. A. (1966)
J. Chem. Phys., *45*, 4493, 4500.

MARKOVNIKOV, V. (1870)
Ann.,*153*, 256.

MORE O'FERRALL, R. A. (1970)
J. Chem. Soc. (B), 274.

ROCHESTER, C. H. (1970)
"Acidity Functions", Academic Press, New York.

ROSS, J. A., SEIDERS, R. P. and LEMAL, D. M. (1976)
J. Amer. Chem. Soc., *98*, 4326.

SALEM, L. (1971)
Accounts Chem. Res., *4*, 322.

SAYTZEFF, A. (1875)
Ann., *179*, 296.

SHORTER, J. (1973)
"Correlation Analysis in Organic Chemistry: An Introduction to Linear Free Energy Relationships", Oxford University Press.

SMITH, P. A. S. and DeWALL (1977)
J. Amer. Chem. Soc., 99, 5751.

STOCK, L. M. and BROWN, H. C. (1963)
Adv. Phys. Org. Chem., 1, 35.

TAFT, R. W., Jr. (1952, 1953)
J. Amer. Chem. Soc., 74, 3120; *75,* 4231.

WISEMAN, J. R. (1967)
J. Amer. Chem. Soc., 89, 5967.

WITT, O. (1876)
Ber. Deut. Chem. Ges., 9, 522.

WOODWARD, R. B. and HOFFMAN, R. (1969)
Angew. Chem. Internat. Edn., 8, 781.

ZIMMERMAN, H. E. (1971)
Accounts Chem. Res., 4, 272.