

# ORGANIC SYNTHESSES UNDER PLASMA CONDITIONS

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## ABSTRACT

Non-equilibrium plasmas offer unique possibilities for chemical syntheses since they allow production of highly excited molecules or gaseous ions in large quantities. Plasma techniques have been applied to carry out various types of isomerizations or eliminations with high yields. It is also possible to generate reactive species (atoms, radicals, carbenes . . .) by these methods and to use them in chemical synthesis.

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Chemists have always been fascinated by electrical discharges and have tried to apply discharge techniques as soon as they became available. Chemical experiments with sparks were reported as early as 1795. Studies using arc and ozonizer discharges were started in the middle of the last century. These experiments showed a number of surprising reactions; however, the yields were very small and the products were contaminated by large quantities of tarry or polymeric material. For this reason practically all the older experiments had no preparative value. A notable exception is of course the synthesis of ozone.

The search for new reactions and unusual reaction conditions has renewed the interest in plasma chemistry in recent years. Some of the new experiments have been quite successful. However, plasma chemistry is still a very new technique and a field full of unsolved problems.

It is the purpose of this paper to review the present state of organic plasma chemistry and to demonstrate preparative applications through typical examples. In addition, some of the elementary processes of organic plasma chemistry will be discussed. Reactions in arc discharges will not be included in this summary.

## BASIC CONSIDERATIONS

The course of a chemical reaction is determined by steric and energetic factors. Reactions will only start if the partners have sufficient energy and collide in a favourable geometry. The necessary energy may be transferred to the molecules in a number of ways.

Conventional energy sources excite translations, rotations and vibrations. If the molecules have gained enough energy they will react (*Figure 1*). Bimolecular reactions start when the partners have gained sufficient vibrational energy and monomolecular reactions are initiated by bond ruptures.

Considerably higher energies would be required for ionizations. Obviously the stepwise activation, which is typical for conventional heat transfer, will never lead to the ionized state of the (uncharged) molecule. It is also not possible by this method to excite molecules beyond the energy required for bond ruptures.

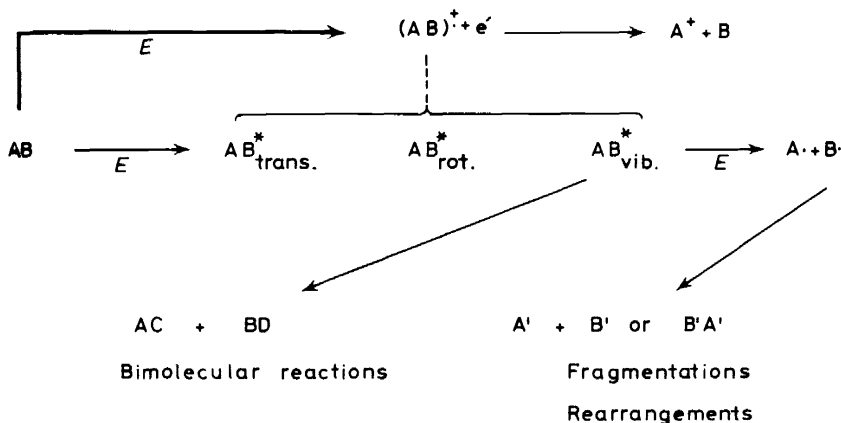


Figure 1. Elementary processes.

The excitations caused by conventional heat sources can also be achieved by electron collisions. Therefore, the results found in high temperature chemistry can also be obtained in plasma chemistry. Both methods, however, differ with respect to deactivation. In high temperature chemistry most molecules have fairly high energies. In plasma chemistry, however, only a few molecules are excited; these may react and afterwards are rapidly deactivated by interaction with other molecules. Thus, plasma chemistry has a quenching mechanism probably more rapid and more efficient than other ways of quenching.

In order to generate radical ions, ions or highly excited molecules it is necessary to transfer larger amounts of energy in single excitation processes (Figure 1). Excitations of this kind with energies up to 5 eV are known from photochemistry. Normally photon absorption transfers the molecules from the ground state to the first electronically excited state. Both states are well defined and the absorbed energy is known accurately. In photochemistry ultra-violet light is normally used for energetic reasons. The range of 220–400 m $\mu$  corresponds to a photon energy of 3–5.5 eV.

It is possible to transfer similar amounts of energy by electron impact. However, since the colliding electrons have a range of energies (e.g. Boltzmann distribution) and various fractions of their energy are transferred in the collisions, the energies of the excited species vary over a wide range.

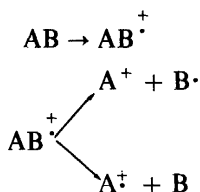
In addition to electron collision, excited molecules may also be formed by recombination between an ion and an electron. In this process the recombination energy of 8–10 eV is distributed between two neutral particles in various proportions. Thus, electron collisions or recombinations can generate the same excited species as photon absorption does and may

initiate the same reactions. However, due to the spread of energies of the excited molecules, plasma chemistry will never reach a selectivity comparable to that of photochemistry.

One of the challenging problems in plasma chemistry is to generate electrons with selected energy ranges. If they were to become available the selectivity of plasma reactions could be greatly increased. An approach to this problem has been made by the SESER experiments<sup>1</sup>. However, in the manner in which these experiments are carried out at present, the zones containing high energy electrons are small compared with the bulk of the plasma and therefore are not suitable for application in preparative plasma chemistry.

The range involving excitation energies between 5–9 eV is not accessible by photochemistry or by conventional heat transfer, but can easily be achieved by electron collisions. In this range highly excited molecules are formed. The chemistry of such species is practically unknown but interesting results are anticipated, since reactions with high energy demand or extreme energies of activation may occur. This area may well become an attractive field for future activities in plasma chemistry.

Collisions with electrons of energies in excess of the ionization potential (8–9 eV for organic molecules) may produce radical ions. If these have enough energy they split forming new radical ions, ions and neutral molecules, e.g.

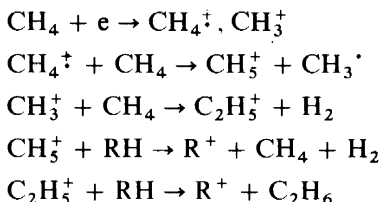


The chemistry of radical ions and ions again is a challenging new field for plasma chemistry. It is generally accepted that various organic compounds will form ions or radical ions under special experimental conditions, e.g. on treatment with sulphuric acid. These ions, however, are not free, but exist as ion pairs or surrounded by a shell of solvent molecules. Solvated ions and radical ions have been studied extensively. However, the chemistry of free ions and radical ions, which is expected to be quite different from that of solvated ions, is practically unknown.

Apart from plasma chemistry the only way to generate free radical ions and ions, is mass spectroscopy. Almost all information available on free ionic species and their tendency to rearrange and split is provided by mass spectroscopic techniques. Though many mass spectra have been published, in general they have been taken with the purpose of structure determinations. Ionizations have been performed with 50–70 eV electrons which cause complicated fragmentation patterns, numerous rearrangements and sometimes the complete scrambling of the atoms within the molecules. Information more applicable to plasma chemistry is supplied from mass spectra taken with ionization energies just above threshold ( $\sim 10$ –15 eV).

Little is known of the reactivity of free radical ions and ions towards

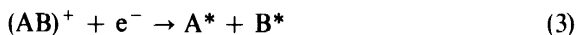
neutrals, except through special mass spectroscopic techniques. In chemical ionization mass spectroscopy<sup>2</sup>, ions are generated and then allowed to react with other molecules. Primary ions normally are derived from methane (CH<sub>4</sub>):



Another source of information on the reactivity of ions towards neutrals is high pressure mass spectroscopy. For example ions of some aromatic molecules readily form complexes with neutral molecules at pressures of 0.1–1 Torr<sup>3</sup>.

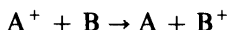
The comparison between mass spectroscopy and plasma chemistry presents a difficult problem. Mass spectroscopy only monitors ions. In plasma chemistry, however, ionic species only exist as reaction intermediates which are neutralized prior to identification. This raises the question whether this neutralization would change the structure of the species.

Several mechanisms of neutralization are possible. The recombination can be three-body collision with the wall or another molecule taking up part of the excess energy (1). For organic molecules which form negative ions or ion-molecule complexes, other mechanisms may be predominant. When a negative ion combines with a positive ion (2) or when an ion-molecule complex traps an electron (3) the energy of neutralization is distributed between two molecules. If the molecules involved are big enough they can, by means of their many modes of vibration, take up considerable amounts of energy without fragmentation.



(Possible A–B\*)

In principle there could be a neutralization between an ion-molecule complex and a negative ion. However, only few compounds readily form ion-molecule complexes and negative ions. Therefore, this recombination process has little importance. Probably the predominant way of neutralization in plasma is a charge transfer reaction:



Such processes are extremely fast and liberate little energy. Thus, it is very unlikely that charge transfer processes change the structure of the molecules. It is also safe to assume for neutralization by three-body collisions or through ion-molecule complexes and negative ions, that many of the molecules survive the neutralization without damage. Consequently, one may expect in plasma chemistry results similar to those in mass spectroscopy. It should also be possible to reproduce processes observed in mass spectroscopy on a

larger scale by plasma chemistry. This would make plasma chemistry a kind of preparative mass spectroscopy. The main difference between the two methods is the pressure, which in mass spectroscopy suppresses bimolecular processes while in plasma chemistry bimolecular processes are extremely important.

Other species which may be present in plasmas in considerable concentrations are negative ions. Their role in plasma chemistry is not quite clear. Negative ions are formed by molecules containing electronegative atoms. The electron affinities of these molecules are small ( $\leq 1$  eV). Therefore, the attachment of a thermal electron does not liberate enough energy to break bonds. Dissociative attachments caused by electrons of higher energy have small cross sections and will not contribute much to the chemistry in plasmas. However, recombination rates may be greatly increased for molecules capable of forming negative ions.

### PLASMA REACTORS

Various plasma reactors have been designed, which apply different types of discharges. The principles of the three most important types (*Figure 2*) will be discussed briefly. In ozonizers high voltage (d.c. or low frequency a.c.) is supplied to metal electrodes which are separated by two layers of insulating material (glass or silica) with a narrow gap between them. Due to the high resistance the current density is low and large surface areas are required for reasonable production rates. Ozonizers are normally operated at atmospheric pressure. The application of ozonizers is more or less restricted to reactions which cause no deposition on the walls, since the large surface and the narrow gaps would impede the cleaning of the equipment.

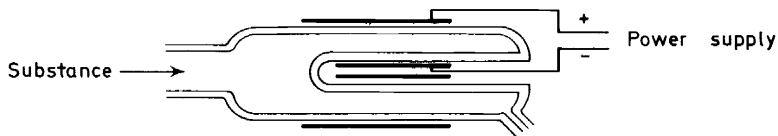
Glow discharges are operated at reduced pressures. The discharge may be generated by metal electrodes which penetrate into the reactor and which are connected to a high voltage source. Often the electrodes have unwanted side effects, since they may catalyse reactions of starting materials, intermediates or products. Furthermore when reactions are carried out with organic substances, the electrodes are rapidly coated with polymeric material, unless they are separated from the reacting gas, e.g. by a zone of inert gas.

The contact between the metal and the plasma is avoided in electrodeless high frequency discharges. In these arrangements high frequency is coupled inductively or capacitively to the plasma. Such setups are very versatile and especially suited for exploratory work. Microwave discharges have also been used in plasma chemistry. However, in most experiments difficulties arise due to the variation of field strength within the reactor. In some parts of the reactor the starting material may be completely decomposed while in other areas it passes the plasma unaffected.

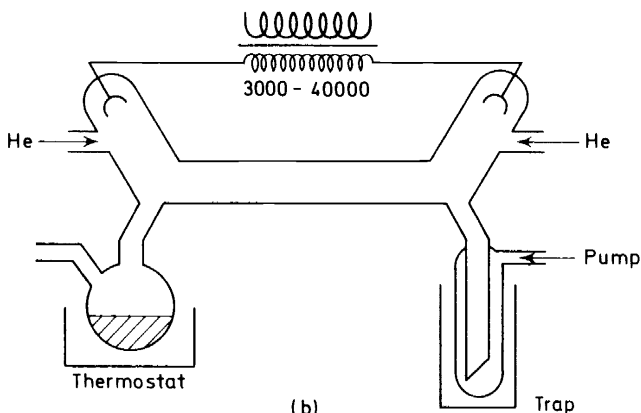
### EXPERIMENTAL CONDITIONS

The experimental conditions for the different reactors vary over a wide range. It is therefore impossible to name typical conditions for experiments in non-equilibrium plasmas. The only features, which are common to all these discharges, are a very low degree of ionization ( $10^{-6}$ - $10^{-5}$ ) and gas temperatures which are not more than a few hundred degrees above ambient.

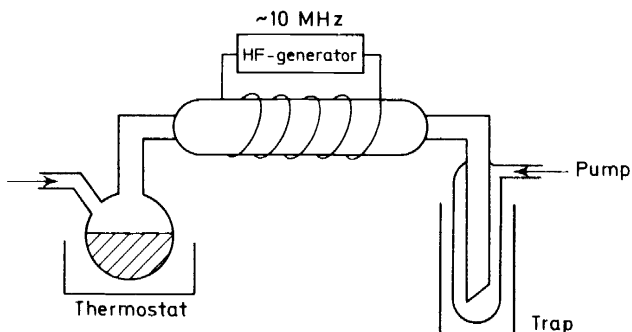
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(a)



(b)



(c)

Figure 2. Reactors of various types: (a) ozonizer, (b) high voltage, and (c) high frequency discharges.

There is at present no agreement on the kind and number of data which should be reported to fully characterize a plasma experiment. It is easy to determine pressure, power consumption and mass throughput. From these data and the geometry of the reactor gas velocities and residence times can be calculated. These data may serve as a guide to reproduce a plasma experiment. Experience, however, shows that usually a few more experiments are still necessary to reach optimum conditions.

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All additional parameters are more difficult to determine. Unfortunately it is not known at present which parameters really are important for the result of plasma experiments. Therefore, it is desirable to get as much information as possible on gas temperatures, electron densities, collision frequencies, electron energies, as well as concentration and the nature of the various charged and neutral particles present in the discharge. Only when the dependence of all the product yields on all these parameters has been studied, will it be possible to decide which parameters are critical and which are not.

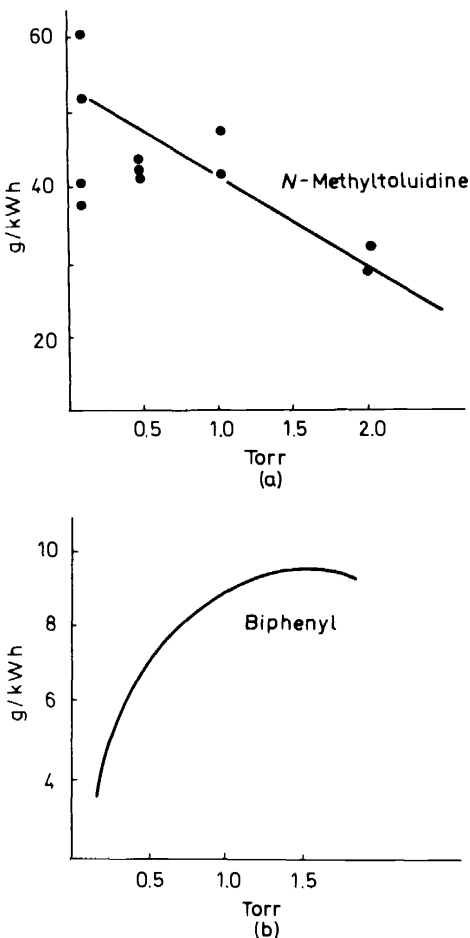


Figure 3. Pressure dependence of the yield. (a) Rearrangement of *N,N*-dimethylaniline to *N*-methyltoluidine. (b) Dimerization of benzene to biphenyl.

Some systematic studies have been made on the influence of pressure and power on the yields. An increase in pressure will lower the mean free path of the electrons and as a consequence their mean energy (constant field strength assumed). This results in fewer inelastic collisions and a smaller chemical

yield. *Figure 3(a)* demonstrates this dependence for a monomolecular reaction. In bimolecular processes there is an opposing effect, since the rate is proportional to pressure. For this reason the yield of bimolecular reactions often passes through a maximum with increasing pressure, *Figure 3(b)*. The dependence of the yield on power has been studied in a few cases only. Normally there is no dependence if the yields are calculated in g/kWh. Occasionally an increase (or decrease) in yield has been observed with increasing power, a result which has not yet been fully explained.

## APPLICATIONS

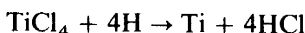
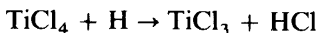
Of the great number of organic substances only a few hundred have been investigated experimentally in plasmas. Very many reactions have been observed in these experiments; however, in general the yields were small and the products contaminated by polymeric materials. Recent experiments demonstrated that only a narrow range of experimental conditions will give satisfying results and yields suitable for preparative applications. In early investigations no systematic studies were carried out to find optimum experimental conditions. Therefore it may be worth while to repeat many of the older experiments, even those which have negative results.

It is not attempted in this summary to list all plasma reactions of organic substances, which look suitable for preparative chemistry. Some of the material has been reviewed recently<sup>4</sup>. In the following paragraphs selected reactions are represented which may be considered as typical for the behaviour of organic molecules in the plasma of glow discharges. Since some of these reaction types are also found for inorganic molecules, a few inorganic examples are also included.

Frequently in plasmas reactive species are formed, which may be stabilized in various ways. Only in rare cases is it possible to generate such species and to study stabilization reactions outside the discharge. Such separation is possible with diatomic gases. Hydrogen, oxygen, nitrogen and the halogens dissociate into atoms if subjected to glow discharges. The rate of recombination is sufficiently slow to allow the atoms to leave the reactor. Since the recombination is catalysed by metals, electrodeless discharges lead to higher atom concentrations than reactors with electrodes (e.g. those of Wood<sup>5</sup>).

The atomic gases readily react with many inorganic and organic compounds. For the investigation of such reactions the separation of the processes of generation of the reactive species and the interaction with other substances is advantageous. However, the same reactions occur when the molecular gases and the trapping agents pass the discharge in common.

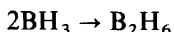
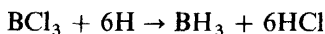
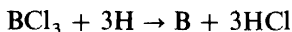
The reductive power of atomic hydrogen has been used in several inorganic systems. Halides like titanium tetrachloride are converted to lower valence states or to the metal<sup>6</sup>:



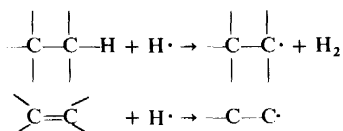
Mixtures of boron trichloride and hydrogen (1 : 5) form the metal in 99.9 per



cent purity. Mixtures in the ratio of 1 : 12 lead to boranes<sup>7</sup>.

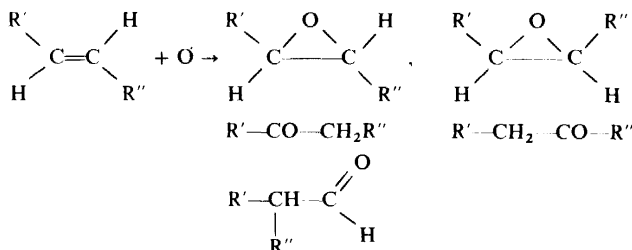


The reaction of atomic hydrogen with organic substances has not been studied systematically and has not yet been applied in preparative chemistry. In all the known reactions between atomic hydrogen and organic substances the results are very simple. Atomic hydrogen reacts with saturated compounds under hydrogen abstraction, and with unsaturated compounds under addition:



Both processes yield radicals. Since atomic hydrogen is easily prepared and its reaction with organic molecules is very effective it seems possible to use atomic hydrogen as a convenient route to preparative radical chemistry.

If atomic oxygen is allowed to react with saturated organic molecules, it abstracts hydrogen and forms radicals. Unsaturated compounds add atomic oxygen with formation of epoxides, which in part rearrange to carbonyl compounds:



Plasma experiments with atomic oxygen have concentrated on the addition to propene and styrene. Propene gave the highest yields of propylene oxide when the hydrocarbon was mixed with oxygen before it entered the discharge<sup>8</sup>. This technique, however, is limited either to very oxygen-rich or to very propene-rich mixtures which are not explosive.

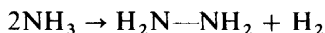
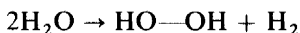
Atomic nitrogen reacts readily with most substances. Organic substances on reaction with atomic nitrogen form mainly hydrogen cyanide. The incorporation of atomic nitrogen into organic molecules has been accomplished only rarely<sup>9</sup>.

A reaction type which is quite common both for inorganic and organic molecules is a dimerization with elimination of atoms or small groups:

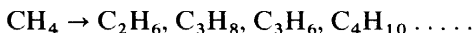
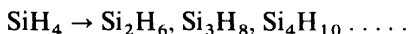


This reaction probably involves several steps, the first being the homolysis of the R—X bond. The radicals R easily dimerize forming R—R. The X fragments also may dimerize but probably stabilize in a more complicated way.

The inorganic reactions of this type which have been studied extensively are the syntheses of hydrogen peroxide and hydrazine:

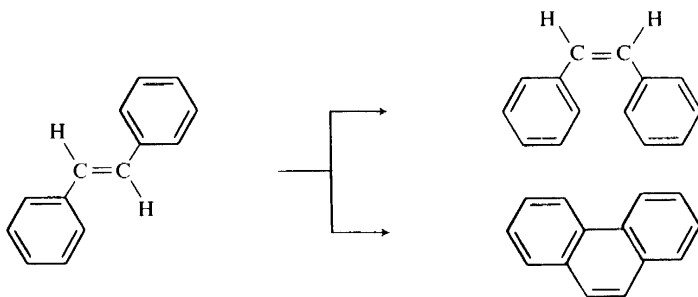


Silanes, germanes, boranes and phosphines also show the dimerization as the main process but they, like saturated hydrocarbons, do not stop at the dimer but also form higher homologues.



Many organic molecules have different groups which may be eliminated and thus would lead to mixtures of products. Neat products are obtained only if all bonds are equal or one elimination requires considerably less energy than all the others. For example, benzene dimerizes to biphenyl contaminated only by a few per cent of triphenyl, the product of a consecutive reaction. Benzylic alcohol may serve as an example for the second possibility. The weakest bond in the molecule is the bond between carbon and oxygen. This is broken almost exclusively and the dimerization to dibenzyl is nearly quantitative.

Another reaction type frequently observed in plasmas is isomerization. A simple example is the *cis/trans* isomerization of olefins. This reaction and its preparative possibilities have been studied for stilbene<sup>10</sup>. When the *trans* isomer is the starting material the product is *cis*-stilbene contaminated by some phenanthrene. At low rates of conversion the contamination is negligible. At higher conversion rates phenanthrene may become the main product.

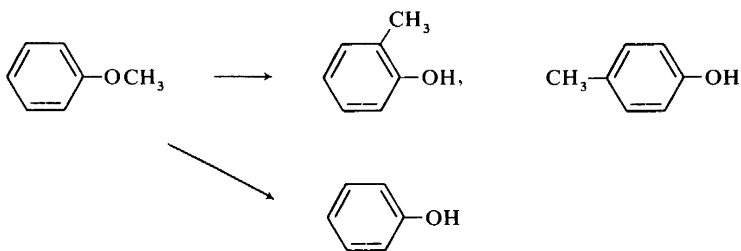


For olefins which polymerize easily the *cis/trans* isomerizations may be overshadowed by polymerization processes.

An isomerization typical for aromatic molecules is the migration of substituents. Such reactions have been studied thoroughly with aromatic ethers<sup>11</sup>. For example, anisole in plasma rearranges to ortho- and para-cresol.

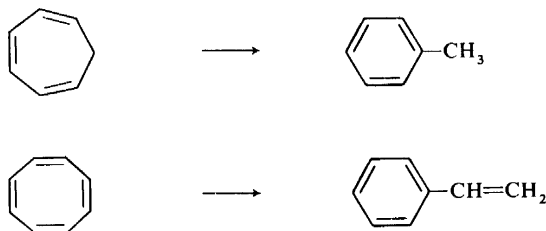
Competing with this rearrangement is always a fragmentation to phenol.

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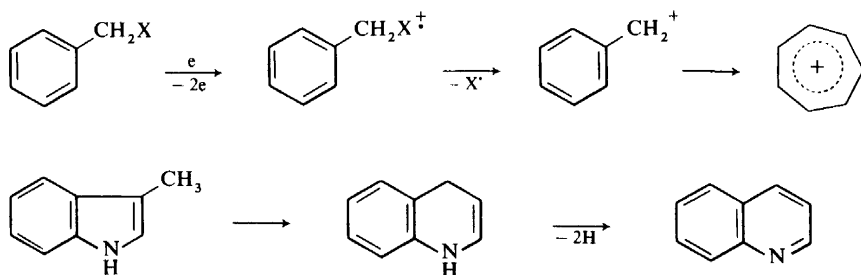


Analogous isomerizations have been observed for various ethers as well as secondary and tertiary amines. The results are always similar. The ortho/para ratio of the rearranged products is practically independent of the experimental conditions, the nature of the starting material, and the migrating group. Over a wide range of power ratings the amount of phenol increases with power. However, even with the lowest possible power the formation of phenol cannot be completely suppressed.

Several rearrangements have been found for cycloolefins. The driving force in these reactions frequently is the tendency to form the more stable aromatic compounds. Thus cycloheptatriene and cyclooctatetraene isomerize easily to toluene and styrene respectively:



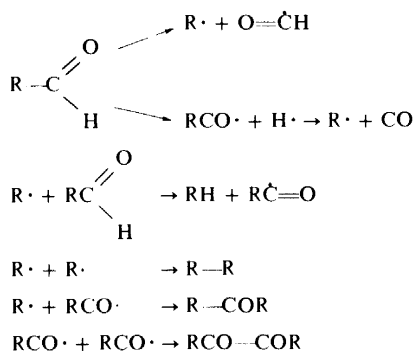
The reverse of the first reaction, the insertion of a methyl group into a benzene ring, which is a typical feature of the mass spectra of toluene and benzylic compounds, has not been observed in plasma chemistry.



The only analogous insertion of a methyl group that has been found is for  $\alpha$ - and  $\beta$ -methyl indole. Here again the tendency to form the more stable heterocyclic six-membered ring favours isomerization. Ring-chain isomerizations have been observed for several cyclic nitrogen compounds. Substances like pyrrole or pyridine rearrange to unsaturated nitriles. The yields of such reactions are often low, since it is difficult to prevent polymerization of the nitriles.

Another reaction type frequently observed for organic substances is elimination. In those plasma reactions which lead to the complete destruction of organic molecules, various eliminations occur. Other eliminations are very useful in preparative chemistry. In these reactions atoms or small groups are eliminated without alteration of the structure of the remaining fragments. The remaining species may be stable molecules or radicals which then by way of the various routes of stabilization form the final products. All groups which are attached to the molecules by relatively weak bonds may be eliminated. Of the various possibilities the eliminations of hydrogen, carbon monoxide and carbon dioxide seem most promising in preparative chemistry. The elimination of hydrogen leads from saturated compounds to olefins and from olefins to acetylenes. In the few cases of plasma dehydrogenation which have been studied, satisfying results could only be obtained within narrow ranges of experimental conditions, since the products generally polymerize easily in plasmas.

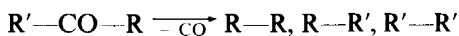
Plasma eliminations of carbon monoxide are very facile reactions. Aldehydes decarbonylate in a reaction involving several steps. The radicals formed as intermediates stabilize by hydrogen abstraction or by dimerization.



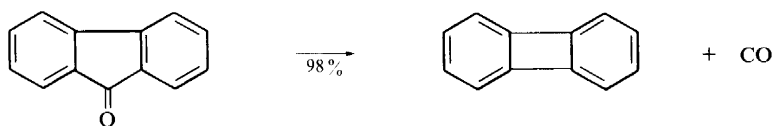
The main product is always the hydrocarbon RH, the predominant byproduct being the dimer R—R. The amounts of ketones and diketones depend strongly on experimental conditions. For example, benzaldehyde at a conversion rate of 50 per cent forms about 80 per cent benzene, 20 per cent biphenyl and approximately one per cent of benzophenone, with traces of benzil. With added argon it was possible to isolate as much as 25 per cent benzophenone and 15 per cent benzil. Other aldehydes show similar results. Even very sensitive substances like thiophene aldehyde may decarbonylate in plasmas without destruction of the heterocyclic ring<sup>12</sup>.

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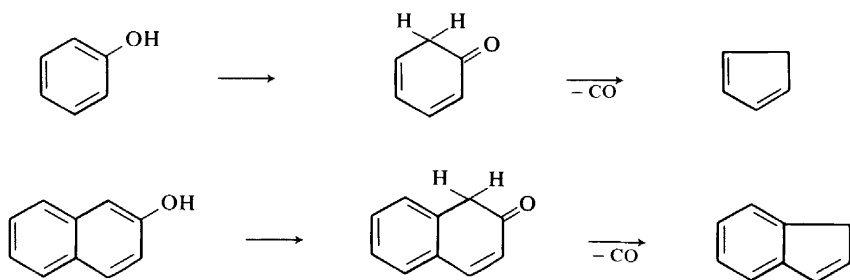
The decarbonylation of symmetrical ketones leads to symmetrical hydrocarbons; that of unsymmetrical ketones to mixtures of hydrocarbons.



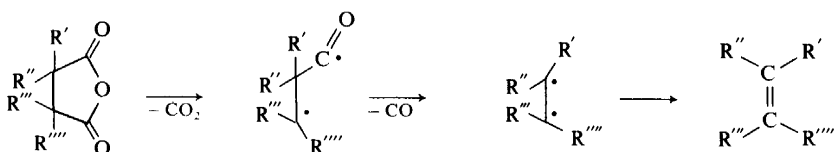
Especially attractive are decarbonylations of cyclic ketones. When, for example, fluorenone is subjected to a glow discharge the only product is biphenylene which is formed almost quantitatively<sup>13</sup>.



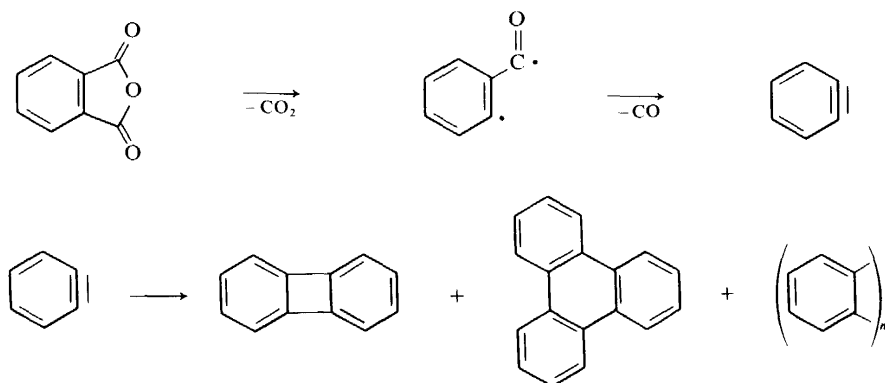
This reaction nicely demonstrates the preparative possibilities of plasma chemistry. Classical methods to prepare biphenylene involve a number of steps, all of which have very low yields. As an alternative, plasma chemistry offers an efficient one-step route. Also suitable for decarbonylations are aromatic hydroxy compounds. These on electron impact probably tautomerize to their respective keto forms which then may lose carbon monoxide. Thus it has been possible to decarbonylate phenol and naphthol to cyclopentadienes and indenenes.



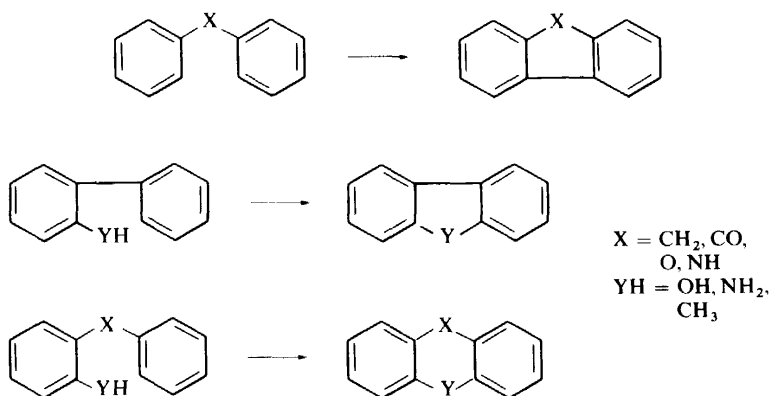
Elimination of carbon dioxide transforms carboxylic acids into radicals which stabilize in the usual ways. Decarboxylation followed by decarbonylation is observed for acid anhydrides. Cyclic anhydrides first form acyl biradicals which then lose carbon monoxide to form a second biradical. This normally stabilizes with formation of a multiple bond.



Saturated anhydrides thus are converted into olefins, unsaturated anhydrides to acetylenes. Bicyclic or tricyclic acid anhydrides split to give the corresponding bicyclic or tricyclic olefins. For example, phthalic anhydride forms the very reactive dehydrobenzene which, in the absence of other compounds, dimerizes, trimerizes or polymerizes.



Products of elimination processes which have a suitable geometry stabilize to cyclic compounds. A series of five- and six-membered rings has been prepared this way:



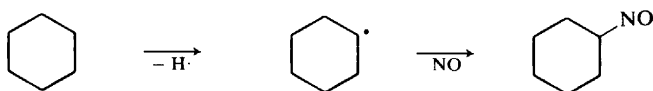
In some cases the cyclization occurs almost quantitatively; in others, it competes with other processes<sup>4</sup>.

In addition to the reactions which are typical for organic substances in glow discharges, there are a number of experimental results for which the range of validity has not yet been determined. Some of these observations will be discussed briefly.

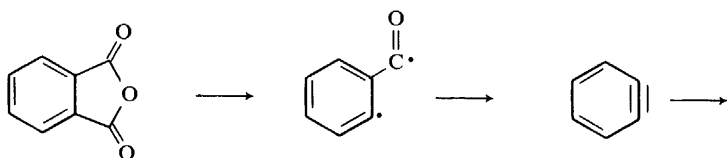
Discharges furnish a new way to generate reactive species which may be trapped by suitable additives. Radicals, for example, can be very effectively

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scavenged by nitric oxide. When mixtures of cyclohexane and nitric oxide are led through a discharge, the cyclohexyl radicals are converted into nitroso cyclohexane<sup>14</sup> which is a starting material for the synthetic polyamide perlon.



More complicated trapping techniques have been applied to phthalic anhydride. This compound fragments in a two-step reaction and in the absence of trapping agents dimerizes in a two-step reaction (or in part trimerizes to triphenylene). It has been possible to trap all three intermediates<sup>15</sup>. Hydrogen, for example, attaches to dehydrobenzene and the diphenyl diradical, acetylene only to the dehydrobenzene. Ammonia adds to all the intermediates.



products† per cent

|                        |   |
|------------------------|---|
| without additives      | benzene 0.5, biphenyl 10, biphenylene 42, triphenylene 19, polymer 100                          |
| with hydrogen          | benzene 5, biphenyl 34, biphenylene 4, triphenylene 8, polymer 24                               |
| with acetylene         | benzene 12, phenylacetylene 31, biphenyl 4, biphenylene 5, polymer 13                           |
| with ammonia           | aniline 13, aminobenzaldehyde 21, carbazole 5, biphenylene —                                    |
| with carbon disulphide | benzene 0.5, biphenyl 8, biphenylene 23, triphenylene 11, dibenzothio-<br>phene 31, polymer 30. |

Especially noteworthy is the trapping by sulphur atoms formed by the fragmentation of carbon disulphide. In this case both reactants are reactive intermediates formed in a plasma reaction. The unexpectedly high yield (30 per cent) proves the efficiency of trapping.

Special activity in plasma chemistry has recently been focused on polymerizations and surface treatments. The earliest surface treatments were performed on metals. These, when exposed to plasmas, may form nitrides, borides, carbides or silicides on the surface depending on the species present in the gas phase. Plasma techniques have also been used to precipitate metals or inorganic compounds from the gas phase and to form conducting

† Liquid products = 100.

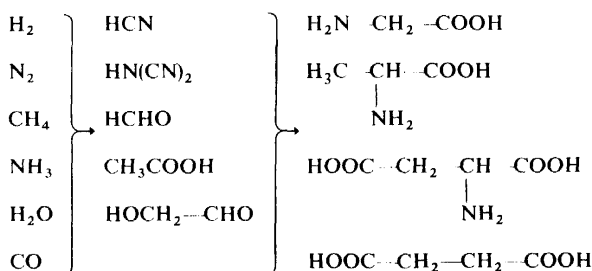
or non-conducting films. Plasma techniques have also been applied for etching or removal of such films.

Surface modifications of organic material can be achieved, when an organic polymer is subjected to a glow discharge. The electrons and possibly also other particles which strike the polymer, generate reactive sites (radicals) on its surface. These reactive sites lead to crosslinking and thus may improve the surface properties, such as adhesion. The reactive sites may also be used to graft to other monomers. By this treatment it is possible to change completely the character of the polymer surface.

Furthermore, it is possible to deposit organic films on various objects by plasma-induced gas phase polymerizations. These techniques are not limited to conventional monomers. Almost any organic substance can be converted into polymerizable material through plasma reactions. It has been possible to produce films of special mechanical, optical, or electrical properties starting from materials which would not polymerize under normal polymerization conditions.

While polymerizations are easily achieved, oligomerizations have been observed only occasionally. For example, acetylene in plasmas easily polymerizes to a high molecular weight material. Under certain experimental conditions the polymer formation is suppressed and only molecules with 4, 6, 8 and 10 carbon atoms are formed. To achieve this change in product formation specially treated solid particles are inserted into the reactor. Though the mechanism is not known, it is probably the enlarged surface which causes a rapid deactivation of reactive species and thus stops the polymerization at an intermediate stage.

A related topic is the synthesis of organic molecules from simple inorganic gases. Experiments of this kind have been performed to study chemical evolution. It is believed that the atmosphere of the primitive earth consisted of simple gases like hydrogen, nitrogen, water, ethane, ammonia and carbon monoxide. If such mixtures are subjected to discharges (sparks, corona or glow discharges) they form larger molecules. For example, carboxylic acids and amino acids have been identified<sup>16</sup>. Under the influence of heat, light or discharges these compounds could form larger molecules which might eventually have become the precursors of living material.



### SPECIAL TECHNIQUES

In some cases modification of plasma techniques has resulted in drastic



changes of the product distribution. Two modifications, the insertion of solid material into the reactor, and the addition of inert gases, have already been mentioned. The effect of the inert gases may be due to a dilution of the reactive species, thus slowing down bimolecular processes and favouring monomolecular reactions. In some systems small additions of argon caused a pronounced increase of the yield, possibly because argon metastable atoms carry energy from electrons to the organic molecules.

Other modifications involve the pulsing of a discharge. By this method sensitive products may be swept out of the reactor before a new discharge starts. In other variations one or more constrictions are introduced into the discharge zone. Behind the constrictions plasma volumes are formed in which the electron energies are shifted to higher values compared with the rest of plasma<sup>1</sup>.

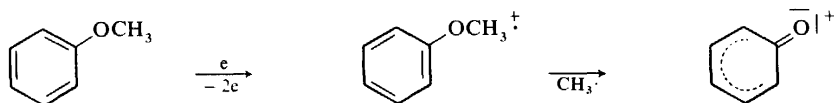
### REACTION MECHANISMS

The study of the mechanisms of plasma reactions is an interesting and very important field. Progress in plasma chemistry definitely depends on extensive mechanistic studies and a better understanding of the elementary processes. The frequently used method of mechanistic interpretation based on the products is very uncertain. However, even this most simple approach has sometimes provided valuable information, for example, in the rearrangement of anisole<sup>11</sup>.

As mentioned previously, anisole forms cresols and phenol. The ortho/para ratio of the cresols is almost constant, while the fraction of phenol grows with increasing power. Less than one per cent of products with an increased number of carbon atoms (methyl anisole or dimethyl phenol) are found.

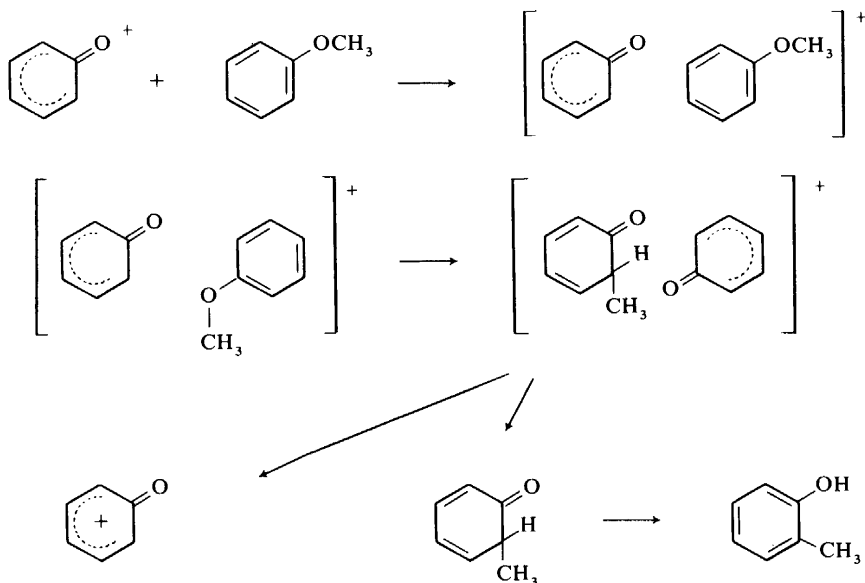
The absence of such compounds rules out all mechanisms which involve the intermolecular attack of free methyl groups, since these would also methylate the starting material or the products. A mechanism involving an intramolecular methylation also seems unlikely since there is no force which would keep the methyl group in the vicinity of the aromatic ring. A concerted breaking of the old with formation of a new bond seems hardly possible for the para position. Thus various mechanisms being ruled out, the migration of the methyl group must occur within a complex of two molecules. The only complexes in the gas phase which have sufficient stability are those between ions and neutrals. Therefore the rearrangement of anisole probably involves ion-molecule complexes.

The power dependence of the phenol yield supplies additional information on the mechanism. This dependence can be explained by the following chain mechanism. The reaction starts with the ionization of anisole and a subsequent fragmentation of the radical ion.



The ion adds to a neutral molecule and within this ion-molecule complex the 'rearrangement' occurs. The methyl group migrates from the oxygen to

the ortho or para position of the ion. The result of this migration is a complex between the ion and an unsaturated ketone. Since this ketone is considerably less basic than anisole the new complex is less stable and disintegrates either spontaneously or on collision with a molecule of anisole. The unsaturated ketone tautomerizes to cresol while the ion again enters the chain:



The chain probably is terminated by a recombination process. If the ion-molecule complex is neutralized, a molecule of anisole and a phenoxy radical are liberated. The radical stabilizes through hydrogen abstraction to phenol. Thus each chain process generates several molecules of cresol but only one molecule of phenol. An increase in power causes a higher electron density and thus would shorten the chains and increase the fraction of phenol among the products. The proposed mechanism can be tested by experiments performed with mixtures of two different ethers. Such tests have been carried out with phenylethyl ether and methyl anisole. In addition to the expected products (three for phenetol and four for methyl anisole) five new products were isolated, which could only have been formed in mixed ion-molecule complexes.

### LIMITATIONS, PROBLEMS AND PERSPECTIVES OF PLASMA CHEMISTRY

Obviously plasma techniques are limited to the gas phase and thus can only be applied to molecules which may be vaporized without decomposition. Another serious restriction is caused by the limited selectivity of plasma reactions. If a molecule contains various reactive groups, the plasma reactions will result in a mixture of products. Unless the separation problems

are simple, this will seriously lessen the use of such reactions. Neat or only slightly contaminated products are obtained only for molecules in which either all bonds are equal or one of the bonds is considerably weaker than all the others. If the difference is in the order of 10 kcal/mole, contaminations by side products can be reduced to negligible amounts.

Besides these two principal limitations there are a number of (hopefully!) only temporary difficulties, which impede present applications of plasma techniques. One of the main problems is the lack of simple diagnostic techniques. This lack has prevented systematic studies on the influence of the various parameters on the chemical yield and it is therefore impossible to decide which of the parameters are really important for the outcome of a plasma experiment. Another handicap is the limited knowledge of elementary processes and reaction mechanisms in a plasma.

Before plasma chemistry can be applied in industry, a number of engineering problems have to be solved. It will be necessary to design better reactors, which use short discharge zones with an even distribution of field strengths and electron energies. It will also be necessary to develop reactors which can handle higher pressures, without increasing gas temperatures to a range which would cause pyrolyses of the organic material. Finally it would be desirable to generate electrons with a non-Boltzmann distribution of electron energies and possibly to increase the selectivity of plasma reactions, or to tailor the discharge to a specific reaction.

From the present situation it is difficult to predict future developments of plasma chemistry. A number of recent results are interesting for preparative chemistry and may also become commercially attractive. These include polymerization reactions, surface treatments and some plasma syntheses of compounds which are fairly valuable and difficult to prepare by classical methods.

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