

THERMOCHEMISTRY - SOME RECENT LINES OF DEVELOPMENT

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Abstract - Developments in calorimetric instrumentation and technique are reviewed with special reference to combustion and vaporization calorimetric measurements. Examples are given of areas of enthalpy of formation determinations that are of particular interest in view of the contributed posters for the thermochemistry section. The particularly rapid developments in thermochemical measurements and interpretation of results on organometallic compounds is discussed. The importance of considering the model of interpretation and prediction in the choice of compounds for study is emphasized.

INTRODUCTION

No matter how one defines "thermochemistry", it represents quite an extensive field. The contents of this lecture will, however, be limited to discussions of some of the present-day activities aimed at establishing enthalpies of formation of pure compounds and to some extent also of species in solution. One of the principal goals of such work is, as we all know, to create a base of "numbers" and "sets-of-rules" that makes it possible to calculate, with the desired accuracy, energy or enthalpy changes for all kinds of reactions or processes that are, or may become, of interest. (Enthalpy data are, of course, vital also for calculations of changes in Gibbs energy and hence predictions of chemical equilibria.)

In order to interpret experimental results in terms of rules for predictions, models are required. The more fundamental a model is, the brighter the prospects should be for success in predicting a great deal from a limited set of experiments. Also, the higher the quality (= accuracy) of the experimental results, the smaller is the number required to develop and refine the model. By providing reliable data for compounds of high relevance to the model the thermochemists ought, in fact, be most efficient in eventually putting themselves out of business!

For hydrocarbons there are now available a number of rather sophisticated semiempirical methods, e.g. the so-called molecular mechanics force-field calculational procedures, that allow calculation of structures and gas-phase enthalpies of formation in good agreement with the experimental results for the majority of the compounds. These methods, or models, work well for many substituted hydrocarbons as well and extensions to further classes of organic substances appears to be limited mostly by the lack of reliable experimental results. Whereas our talents for interpretation and prediction of bonding and interaction energies for organic compounds are thus reasonably good, such competence with regard to e.g. organometallics is just beginning to emerge. At present, interpretation of thermochemical quantities for organometallic compounds in terms of "transferability" of bond energies is a central theme. How to estimate, from the thermochemical results, the strength of metal to metal multiple bonds in metalorganics is another key question. Clearly, there is a need for many more good-quality thermochemical data, ideally hand in hand with structural information, before real progress in model development can be made. The availability of a large variety of easy-to-operate calorimetric instruments ought to allow the thermochemist to choose for study those organometallic compounds that provide most really new thermochemical information. Awareness of all the "tricks of the trade" in both organic and inorganic thermochemistry should be one of the most valuable tools.

SOME RECENT DEVELOPMENTS OF APPARATUS AND TECHNIQUE

Oxygen bomb combustion calorimetry can be labelled as the "high-way" for obtaining enthalpies of formation of organic compounds. The development of rotating-bomb calorimeters increased the applicability of the technique considerably, mainly because it allows introduction of rather large amounts of some suitable bomb liquid (solution), which upon rotation of the bomb reacts with ill-defined or complex combustion products, bringing them all to some well-defined final state(s). Over the years, several such calorimeters have been developed and described; cf. for instance Ref. 1. Here I will draw your attention to a rotating-bomb calorimeter with some rather interesting features. It was developed quite recently by Hajiev *et al.* in the USSR (2) and combines the advantages of a stirred-liquid and an aneroid calorimeter. The stainless-steel spherical bomb constitutes the inner wall of an hermetically sealed, likewise spherical, shell containing the calorimeter liquid and equipped with an efficient stirrer. This stirrer is driven through a magnet and the whole calorimeter, together with the surrounding constant-temperature thermostat, can be rotated simultaneously around two perpendicular axes. Besides having a constant heat capacity, the sealed system ("block") eliminates possible errors from evaporation of calorimeter liquid. The stirred liquid provides rapid thermal equilibration of the calorimeter, in contrast to metal-block calorimeters. Furthermore, the heat capacity of the calorimeter liquid, n-nonane, is only one third of that of water, resulting in increased temperature change response of the calorimeter. With a bomb volume of 316 cm³ this calorimeter belongs in the macro-bomb calorimeter category.

Many of the most interesting organic "key compounds" have rather complex structures and are often difficult - or impossible economically - to prepare and purify in amounts large enough for conventional macro-bomb combustion studies. Miniaturization of bomb combustion calorimeters has therefore become an important line of development; cf. (3-5) and references listed there. Mini-bomb combustions on samples around 10 mg of well-behaved compounds can give results with a precision comparable to those on a macro scale; cf. Table 1. Determination of mass and ascertainment of complete combustion are the crucial parts of such measurements. The limiting factors in reduction of sample size in combustion studies are indeed requirements with regard to determination of amount of reaction and analyses of combustion products - not the calorimetry as such.

TABLE 1. Examples of calibration of a mini-bomb calorimeter by combustion of benzoic acid

n	m(b.a.) /mg	{ε(calor) ± s̄} / J K ⁻¹	
7	10.8 to 13.5	605.087 ± 0.040	(±0.007 %)
5	10.5 to 12.0	604.862 ± 0.029	(±0.005 %)

The calorimetric system was not exactly the same in the two series of measurement.

Two miniature rotating-bomb combustion calorimeters have been presented lately. One is reported to be built on the design principles of the Bartlesville (macro) rotating-bomb calorimeter (6) and is equipped with a platinum-lined bomb (internal volume 28 cm³) intended for sample sizes of 50 mg or more (7). The other (8), shown schematically in Fig. 1, is an aneroid system with helium gas circulating past the bomb and through channels in the copper block, facilitating heat transfer from the bomb to the block and within the block, thereby reducing the thermal equilibration time to about 20 min. The internal volume of the bomb is 18 cm³ and the rotation motor, directly coupled to the bomb, is an integral part of the calorimeter. - In sharp contrast to the "minis" large-sample-capacity combustion calorimeters ("maxis") have been developed at the National Bureau of Standards (US) for studies of 25 g samples of pure compounds and heterogeneous fuels (9).

Ascertaining satisfactory enclosure of volatile, hygroscopic and/or oxygen-sensitive materials prior to initiation of the bomb reaction is an important

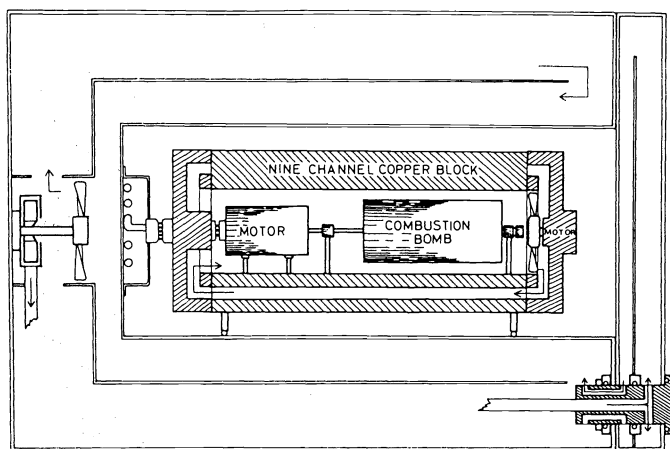


Fig. 1.

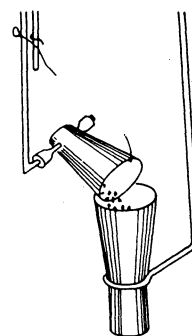


Fig. 2.

part of combustion calorimetric experiments. Erastov and Kolesov (10) have described a technique that allowed them to measure the energy of combustion of liquid trifluorochloroethene (boiling at 246 K). The liquid sample was contained, prior to combustion, in a special-type 0.4 cm³ heavy-walled (10.5 g) platinum crucible sealed by a polyethene lid clamped in place with a platinum nut. To minimize the small amount of soot left on the inner wall of the crucible after combustion the initial pressure of oxygen was increased from the customary 3.2 MPa to as much as 4.65 MPa.

Bomb combustion calorimetry using fluorine as oxidant instead of oxygen has been a well established technique for nearly two decades (11). The extreme reactivity of fluorine has made it possible to study compounds that are more or less unreactive in other oxidants. Leonidov et al. (12) have now described a technique where fluorination is achieved using crystalline xenon difluoride as oxidant. Initially the xenon difluoride is kept in its own Monel crucible (upper crucible; Fig. 2) well separated from the sample to be fluorinated (lower crucible). A thin platinum wire keeps the upper crucible in an upright position. To initiate the reaction the platinum wire is burned through, whereby the upper crucible topples over, spilling the xenon difluoride into the lower crucible. The reaction studied was



yielding $-(163.2 \pm 1.3)$ kJ/mol for the enthalpy of formation of crystalline xenon difluoride, in good agreement with results from reaction of xenon difluoride with phosphorous trifluoride gas (13). One part of the poster (1.12) presenting some of the current work at Argonne describes calorimetric measurements on another, newly synthesized, powerful oxidizer and fluorinating agent, cesium fluoroxysulfate, claimed to be only slightly less powerful than fluorine, xenon difluoride and oxygen fluoride (14).

A newly developed versatile solution calorimeter system is described in poster 1.22 by Professor Shen from Northwestern University in Xian. The system utilizes the technique of refrigeration by semiconductors in controlling the temperature of the surroundings, which together with an efficient stirrer gives a thermostat with low thermal lag. The system, equipped with various interchangeable calorimetric units, can be operated quite satisfactorily in the adiabatic as well as in the isoperibol mode.

In poster 1.9 enthalpies of vaporization are presented together with expansivities for some oxa- and thiaalkanes. For some of the enthalpy of vaporization measurements a newly designed vaporization calorimeter has been used (15). It is based on a twin heat-conduction microcalorimeter system and is equipped with two types of cell-volumes, 0.36 and 0.80 cm³, respectively - for substances with vapour pressures from 10 kPa down to about 17 Pa at 298 K.

The Calvet microcalorimeter is now rather widely used for vaporization and sublimation calorimetric studies. The Osaka group (16) has used such a system in their development of a sublimation calorimeter working in the temperature range from ambient to 450 K for saturation vapour pressures of 1 to 400 Pa. Three different Knudsen-type sample containers are used, two of them equipped

with stoppers that can be manipulated under vacuum from the outside. It is pointed out that for the unstoppered cell ($\Delta p \neq 0$) the $V\Delta p$ correction term (17) may not vanish completely even though a twin system is used. - Skinner *et al.* have indeed made good use of a Calvet high-temperature twin microcalorimeter for sublimation and vaporization measurements on organometallics, but their technique is different (18). They "drop" the sample (3 to 10 mg), contained in a thin capillary tube, and an empty capillary tube into the twin cells and measure the enthalpy change for $A(s \text{ or } l, 298K) \rightarrow A(s \text{ or } l, T)$. Vacuum is then applied to both cells and the enthalpy of sublimation or vaporization at the temperature T is measured. To obtain the sublimation or vaporization enthalpy at 298 K $\{H(T) - H(298 K)\}$ for $A(g)$ must be subtracted from the sum of the two measured enthalpy changes.

In 1977 de Kruif and van Ginkel (19) described a combined torsion- and weighing-effusion apparatus that has since been used for vapour pressure measurements as a function of temperature on a variety of organic compounds. In connection with a report on measurements on the solids of the four lower n-alkanoic acids (20), where dimerization in the gas phase is significant, it was pointed out that the two quantities $p(\text{torsion})$ and $p(\text{mass loss})$ are both related to the monomer/dimer ratio of the vapour phase but in a slightly different manner. As a result, combination of the two sets of measurements permits determination of the monomer/dimer ratio of the gas phase as well as the enthalpy of sublimation. - In poster 1.3 a torsion-weighing effusion instrument similar to that of de Kruif and van Ginkel is reported on. Attention has here been focused on the importance of correcting for hole thickness and size and mean free path of the effusing molecules when evaluating absolute pressures from the measured quantities.

The availability of reasonably priced, high-resolution electronic instruments (digital voltmeters, timers, constant-current and -voltage supplies, etc.) and of inexpensive microprocessors has made automation of data-taking one of the most common lines of instrument development. The torsion-weighing effusion apparatus presented in poster 1.3 has e.g. "automatic taking of results". The LKB 8700 reaction calorimeter, used for the enthalpy of wetting measurements presented in poster 1.4, has been equipped with instruments that permit automatic registration of thermistor resistance values at preselected times. After conversion of resistances to temperatures the stored time-temperature information can be processed automatically to yield the so-called corrected temperature rise. Combined with other quantities stored this then permits automatic calculation of the enthalpy of wetting.

EXAMPLES OF RECENT MEASUREMENTS OF ENTHALPIES OF FORMATION

Inorganic compounds

There are only two contributions to the thermochemistry section concerned with determinations of enthalpies of formation (at 298 K) of inorganic compounds or species. That does not mean, however, that work in this area is not both lively and diversified. The combination of fluorine bomb combustion and reaction-solution calorimetry is extremely powerful in systematic investigations of the thermochemical properties of whole groups of compounds. This is e.g. demonstrated quite nicely in recent work on uranium compounds carried out in cooperation between the laboratories at Argonne and Los Alamos in the USA and the Cordfunke group in the Netherlands. Systems studied in the last few years are, among others, compounds of uranium: uranium + fluorine (21, 22), uranium + chlorine (23), uranium + nitrogen (24), uranium + oxygen (25), uranium + oxygen + fluorine (26), uranium + oxygen + alkali metal (27, 28), etc. - An old solution calorimetric determination of the enthalpy of formation (at 298.15 K) of crystalline uranium tetrafluoride by Hu *et al.* (Academia Sinica) was published in 1980 (29). Their result is given as $-(1894.5 \pm 7.5)$ kJ/mol. The results reported in Ref. 21 and 22 are $-(1920.0 \pm 3.7)$ and $-(1910.6 \pm 2.0)$ kJ/mol, respectively. - In poster 1.12 solution calorimetric work on silver(I)uranium(V)fluoride is described. The implications of the results in relation to the thermal stability of the compound are discussed.

Another example of fluorine bomb calorimetric measurements is the determination of enthalpies of formation of various rare-earth trifluorides carried out at Argonne (30) and in Kyoto (e.g. Ref. 31 and 32). A chlorine bomb combustion calorimetric study was undertaken by Galchenko and his co-workers (33) to establish a reliable value for the enthalpy of formation of niobium pentachloride. A special microfurnace was used to initiate the chlorination process. It was used also for calibration of the system.

I must confess that I was particularly pleased when I received the abstract for poster 1.11 because at that time I was looking for a reliable value for the standard enthalpy of formation of the nitrite ion in aqueous solution.

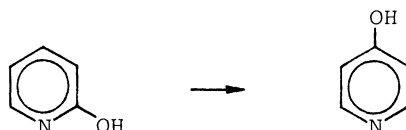
TABLE 2. Destabilization energies for disubstituted benzenes $C_6H_4X_2$

Isomer	$E_{\text{destab}} / \text{kJ mol}^{-1}$			
	X =	CN	Cl	F
1,2-		12.8	10.4	21.2
1,3-		8.0	6.2	5.7
1,4-		2.4	2.9	8.4

The work presented in the poster from the Institute for High Temperatures in Moscow is one of numerous examples of compiler-initiated projects carried through to fill in gaps or resolve discrepancies in existing values for key compounds or species. Similar work has over the years been carried out at the National Bureau of Standards in Washington, D.C.

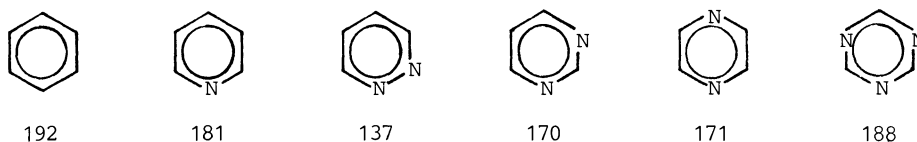
Organic compounds

At present, there seems to be a revived interest in the thermochemistry of organic nitrogen compounds. Gas-phase enthalpies of formation have e.g. recently been determined for a number of diazenes (34,35), two open-chain diazene N-oxides (36), piperazine and azacycloheptane (37), some sterically hindered amines (38), the dicyanobenzenes (39), the hydroxy- and hydroxy-2-methyl pyridines (40), N,N-dimethylaniline (41), the 3- and 4-nitroanilines (42) and 1,3,5-triazine (43). Let us look briefly at some of the results. The gas-phase enthalpies of formation obtained for 1,2-, 1,3- and 1,4-dicyanobenzene were (367.5 ± 1.9) , (362.7 ± 2.0) and (357.1 ± 1.9) kJ/mol, respectively. If the enthalpy increment in going from benzene to cyano-benzene, 135.9 kJ/mol, is assumed to be transferable, the enthalpy of formation of a hypothetical "non-destabilized" dicyanobenzene would be 354.7 kJ/mol. Comparison with the experimental results yield the destabilization energies listed in Table 2. Correspondingly calculated destabilization energies for the dichloro- and difluorobenzenes are also listed in Table 2. Ab initio MO calculations (44) had predicted that for the dicyano- and difluorobenzenes there would be an increase in total energy for the isomers in the sequence 1,3-, 1,4-, 1,2-, with energy increments equal to 0.67 and 2.72 kJ/mol for the dicyanobenzenes and 62.9 and 95.4 kJ/mol for the difluorobenzenes! A more successful prediction of an isomer energy difference was made by del Bene for the hydroxypyridines. In 1979 he performed ab initio calculations on 2- and 4-substituted pyridines (45), at a time when no experimental values for the hydroxypyridines were available. For the isomerization



an enthalpy change of 25.9 kJ/mol was predicted. The value calculated from the experimental results is (38.9 ± 2.6) kJ/mol.

When Tjebbes published his work on the three isomeric diazenes, pyridazine, pyrimidine and pyrazine (46), he also made an attempt to estimate stabilization energies for the compounds in the series benzene, pyridine, diazenes. The results were, however, rather puzzling as pyridazine (1,2-diazene) was shown to be more stable than the 1,3- and 1,4-diazenes, something that was not compatible with chemical evidence. Furthermore, the large decrease in stabilization upon substitution of $-CH=$ by $-N=$ implied a destabilization for 1,3,5-triazine, a compound for which no experimental value was available. It was argued that this might all be a consequence of errors in the bond energies used in the calculations. That has, in fact, been shown to have been the case. Now that most of the required bond energy terms can be derived from reliable experimental values on relevant compounds, the expected trend in the calculated stabilization energies for the diazenes is observed (43). Replacement of $-CH=$ by $-N=$ is demonstrated to have almost insignificant influence on the calculated stabilization energies. The derived values are (in kJ/mol)



It should be pointed out that the uncertainty in the bond energy term $E(C=N)$ is still large - in the order of 3 to 5 kJ/mol.

The current interest in nitrogen-containing organic compounds is reflected in the poster contributions to the thermochemistry section. No less than eight of them describe work that involves organic nitrogen compounds. Gas-phase enthalpies of formation are reported in posters 1.1, 1.13, 1.16 and 1.18. The Osaka group has made a systematic study of the influence of "neighbouring" (CO-N) groups on the total stabilization energies in compounds such as acetyl-urea, malonamide, dimethyluracil and trimethyl isocyanurate (1.16). Combustion and "sublimation" studies at Manchester (1.13) have yielded enthalpy values for gaseous dialkyl dithiocarbamic acids, despite the fact that such compounds are highly unstable in the condensed state. The Bartlesville project intended to provide much needed thermodynamic data for compounds found in coal, oil shale and heavy fractions of petroleum includes calorimetric measurements on nitrogen analogues of the large condensed-ring carbon-hydrogen compounds (1.18).

Thermochemical studies of cyclic *cis*- and acyclic *trans*-azoxy compounds (Diazene N-oxide; 1.1 and Ref. 36,47) have been combined with development of a force-field for molecular mechanics calculations (48) to allow reliable predictions of enthalpies of formation of azoxy compounds not studied experimentally. Strain energies have been derived for the cyclic azo N-oxides primarily for the purpose of comparing them with strain in their azo ($-N=N-$) counterparts (47,48).

In poster 1.6 oxygen-bomb combustion measurements on L-alanine are reported. (Domalski has pointed out (49) that the old measurements by Huffman, Ellis and Fox, reported on D-alanine, probably were performed on a sample that had the L-configuration.) - Reaction calorimetric studies of the condensation reaction of monoethylamine with formic acid yielding 1,3,5-triethyl-hexahydro-s-triazene are described in poster 1.20. - The reaction-solution calorimetric work described in poster 1.7 is directed towards determination of enthalpies of neutralization required for practical applications. The enthalpy of wetting measurements reported in poster 1.4 were aimed at characterizing the surface properties of a certain pigment.

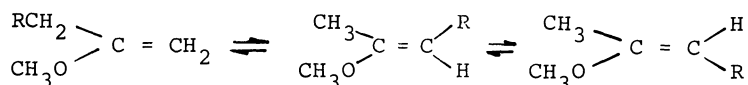
Steele *et al.*, in most of their publications on experimental enthalpies of formation for cyclic carbon-hydrogen and carbon-hydrogen-oxygen compounds, compare their results with values obtained by molecular mechanics force-field calculations (50-52). In poster 1.10 a particularly interesting example of such a comparison on a "key compound" is given. Prediction of the enthalpy of formation of a compound such as tri-*t*-butyl methanol presents a real challenge and agreement (or disagreement) between the experimental result and those derived using different force-fields should provide rather decisive information about the quality and general applicability of the various force-fields presently used.

There are two examples in this section of studies of some special group of compounds carried out systematically over long periods of time. One is the work by Colomina *et al.* on substituted benzoic acids, *e.g.* the dimethyl-, trimethyl-, tetramethyl-, ethyl-, isopropyl-, tertiary butyl-, methoxy-, dimethoxy- and hydroxybenzoic acids, the most recently published study being that on five dimethoxybenzoic acids (53). In poster 1.5 old and new work on the ortho, meta and para methyl- and ethylbenzoic acids is summarized and the results discussed in terms of agreement with predicted values.

The second example is the extensive work by Kolesov *et al.* on fluoro-organic compounds. Studies on interactions between fluorine and oxygen-containing groups have been summarized (*e.g.* Ref. 54). Recently, enthalpies of formation of trifluorochloroethene (10), 1,1,2-trifluoro-1,2,2-trichloroethane (55) and two trifluorochlorobromoethanes (56) were published (for further references *cf.* the publications referred to above). Work on numerous other compounds of this general type has been carried out lately, evident from impressive listings in the latest issue of the Bulletin of Chemical Thermodynamics. The accumulated thermochemical results on fluoro-organic compounds are summarized in poster 1.8.

A number of investigations have been carried out at the University of Turku on isomer equilibria of substituted vinyl ethers. By a gas chromatographic

technique equilibrium constants have been determined as functions of temperature for systems such as (Ref. 57)



yielding values for the enthalpy difference between the isomers. The ability of alkyl groups to stabilize the olefinic system in vinyl ethers has been studied for compounds with varying degree of alkyl substitution of the double bond. Poster 1.21 presents similar work on substituted vinyl thioethers (vinyl sulphides).

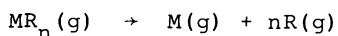
Organometallic compounds

A review article by Pilcher in 1975 (58) included a list of existing enthalpies of formation for organometallic compounds, where 256 values for substances in the condensed state and 192 gas-phase values were quoted. In the most recent review article by Pilcher and Skinner on the same subject (59), with the literature surveyed through 1979, a similar compilation lists 370 condensed-phase enthalpies of formation and 294 gas-phase values. By far the largest increase is for the group VIA organometallics (chromium, molybdenum and tungsten). This reflects present activities in preparing compounds of the transition metals with a great variety in the types of chemical binding between the metal and ligand.

In thermochemical studies of metalorganics combustion calorimetry, at least at the present time, plays a less prominent role than it does e.g. in studies of organic compounds. The main difficulty is to get the chemistry of the combustion reaction "right" for the organic part and the metal under the same bomb conditions. The rather gentle movement of a rotating bomb is not always sufficient to bring to completion, within a reasonable time, additional reaction(s) between an ill-defined combustion product and some bomb solution. Suitable enclosure for combustion of reactive compounds presents another obstacle. - A survey and thorough discussions of advantages and shortcomings of the calorimetric techniques employed in studies of organometallic compounds can be found in the review articles already mentioned (58,59).

One of the principal aims of thermochemical studies of organometallics is to establish "bond energy contributions" of metal-ligand bonds and to examine their transferability. Trends in such "bond energy contributions" with change of metal are, of course, also of prime interest. There are various measures of these "bond energy contributions" and it is important to recognize and distinguish between them.

From the enthalpy of atomization for a poly-atomic molecule MX_n in the gaseous state the 'mean bond dissociation enthalpy' is derived as $\Delta H_a^\circ/n = \bar{D}(\text{M-X})$, provided all the (M-X) bonds are equivalent. For a molecule MR_n (again with equivalent (M-R) bonds), where R is a radical, the enthalpy of the disruption reaction



is given by

$$\Delta H_{\text{disrupt}}^\circ = \Delta H_f^\circ(\text{M}, \text{g}) + n\Delta H_f^\circ(\text{R}, \text{g}) - \Delta H_f^\circ(\text{MR}_n, \text{g})$$

The quantity $\Delta H_{\text{disrupt}}^\circ/n = \bar{D}(\text{M-R})$ is properly termed the 'mean bond disruption enthalpy'. The $\bar{D}(\text{M-R})$ values include possible enthalpies of reorganization of the radicals. To circumvent this, the enthalpies of atomization for $\text{MR}_n(\text{g})$ can be derived and apportioned among all the bonds of the MR_n molecule. Values obtained in this way are termed 'bond enthalpy contributions' and symbolized $E(\text{M-X})$. The $E(\text{M-X})$ values depend on the distribution rules of the scheme adopted in apportioning the enthalpy of atomization among the bonds in MR_n .

The question of transferability of $\bar{D}(\text{M-R})$ values is demonstrated most easily on mixed complexes. If these terms are indeed transferable, the redistribution reaction should be thermoneutral. The transferability problem becomes particularly acute in evaluations of the strength of the metal-metal multiple bonds in transition metal complexes. Hexa(dimethylamido)dimolybdenum is e.g.

a drastic example in that an error in $\bar{D}(\text{Mo-NMe}_2)$ enters sixfold into the derived value for $D(\text{Mo}\equiv\text{Mo})$. Depending on the choice of a "transferable" $\bar{D}(\text{Mo-NMe}_2)$ term, estimates of $D(\text{Mo}\equiv\text{Mo})$ range from 396 to 788 kJ/mol (60,61). - In addition to ambiguities in the choice of $\bar{D}(\text{M-R})$ values deriving from changes in the oxidation and valence numbers for the metal, steric crowding in the MR_n molecule may make the $\bar{D}(\text{M-R})$ value non-transferable.

In the reaction-calorimetric study of some cyclopentadienyl complexes of molybdenum and tungsten, reported on in poster 1.2, efforts have been made to calculate the reorganization enthalpies of the metal-bis(cyclopentadienyl) fragments. These enthalpies, as expected, depend strongly on the angle between the planes of the cyclopentadienyl ligands in the complexes. In poster 1.17 microcalorimetric thermal decomposition and sublimation measurements on various organo-platinum compounds, R_2PtCl_2 , are described. The results have been used to derive bond enthalpy contributions for the (Pt-R) bonds. Crystalline-state enthalpies of formation, obtained from reaction-solution calorimetric measurements on hexafluoroacetylacetonates dihydrated of nickel, cobalt and manganese, are given in poster 1.14 together with enthalpies of dissociation from microcalorimetric studies of the complexes. Metal(II)-oxygen mean dissociation enthalpies have been calculated.

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LIST OF POSTERS IN SECTION 1: THERMOCHEMISTRY

- 1.1 K. Byström (Lund): A calorimetric study of the stability of azoxy compounds.
- 1.2 M.J. Calhorda, A.R. Dias, J.A. Martinho Simões and M.E. Minas da Piedade (Lisbon): Standard enthalpies of formation of $\text{M}(\eta\text{-C}_5\text{H}_5)_2(\text{H})\text{I}$ complexes (M=Mo,W).
- 1.3 G. Cameron, G. Keenan and W.V. Steele (Stirling): A torsion-weighing effusion apparatus for the measurement of the vapour pressures of organic and organometallic compounds in the range 1 to 10 Pa.
- 1.4 A. Charlton and J.I. MacNab (ICI Manchester): Enthalpies of wetting using an LKB calorimeter and on-line data processing.
- 1.5 M. Colomina, P. Jimenez, M.V. Roux and C. Turrion (Madrid): Thermochemical properties of the ortho-, meta-, and para-alkyl benzoic acids.
- 1.6 J. Contineanu and D.I. Marchidan (Bucharest): The enthalpies of combustion and formation of L-alanine.
- 1.7 J.A. Joy and J.I. MacNab (ICI Manchester): Enthalpies of neutralisation of substituted phenols and organic bases by aqueous sodium hydroxide and sulphuric acid.
- 1.8 V.P. Kolesov (Moscow): Thermochemistry of fluoro-organic compounds.
- 1.9 K. Kusano, Y. Saito and M. Shimizu (Miyazaki): Enthalpies of vaporization and expansivities of oxyalkanes and thioalkanes at 298.15 K.
- 1.10 H. Maskill and W.V. Steele (Stirling): A thermochemical study of tri-tert butyl methanol.
- 1.11 V.A. Medvedev, M.E. Efimov, M.I. Smoliar and I.V. Khrenova (Moscow): The standard enthalpy of formation of nitrite ion in aqueous solution.
- 1.12 P.A.G. O'Hare, H.E. Flotow, E.H. Appelman and J.G. Malm (Argonne): New calorimetric studies of inorganic fluorine compounds.
- 1.13 A.M.V. Reis, M.A.V. Ribeiro da Silva and G. Pilcher (Oporto, Manchester): Thermochemical studies on dialkylammonium dialkyl dithiocarbamates.
- 1.14 M.A.V. Ribeiro da Silva, Maria Luísa C.C.H. Ferrao, H.A. Skinner, G. Pilcher and R.J. Irving (Oporto, Manchester, Guildford): Thermochemistry of metal(II)hexafluoro acetylacetonates dihydrated.
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II: A new versatile semiconductor calorimetric system for solution chemistry.

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