

Mass Spectrometry—Volume 5

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A Specialist Periodical Report

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# Mass Spectrometry

Volume 5

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# Foreword

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The present volume with its decennial index is perhaps a suitable occasion to mark the retirement of several stalwarts from this series of Specialist Reports with an expression of sincere gratitude for the efforts they have put into their past and present contributions. In this respect, I surely speak on behalf of all our readership and not just myself. The diligence, flair, and sheer hard work necessary to produce a readable, scientifically accurate coverage of specialists' research areas within the short time-limits set is never financially over-rewarding but our contributors have the benefit of knowing the value of the service they provide to practitioners of mass spectrometry is acknowledged, if sometimes only silently or tacitly.

Blair McMaster's work has taken him largely out of mass spectrometry and, in the interim, I have acted as stand-in until Professor T. Baer takes over the chapter on theoretical aspects in Volume 6. It remains to be seen whether I have exacted the same standards from myself as those set for the other contributors. John Wilson's regular feature on ionization methods has ended and been incorporated mostly into Chapters 1, 2, and 5. The mantle of Charles Brooks and Brian Middleditch has been passed to Fred Mellon who moves on from computers to report gas chromatography-mass spectrometry. His place for Volume 6 is taken by Don Sedgwick who will extend the review on computer applications to include the increasingly important use of microprocessor technology in mass spectrometry. Trevor Spalding has landed a tenured appointment and asked to be relieved as a contributor, at least until he has settled into his new job. John Bowie's contribution on functional group analysis will be dropped by mutual agreement but I am pleased to record he intends continuing to write on negative ion work.

The coverage of mass spectrometry by this Specialist Report, restricted as it is in size, has been necessarily somewhat selective. I am conscious of the inadequate reporting of several developed and developing areas in mass spectrometry which are important but of less widespread general interest. To overcome this inadequacy, the inclusion of brief, special reviews will be continued and extended, particularly as they seem to be well-received. There are four in this Volume, on photoelectron-photoion coincidence spectroscopy and on uses of mass spectrometry in geochemistry, environmental sciences, and food technology. For Volume 6, it is hoped to include features on secondary ion emission and ion beam experiments.

Our readers may be interested to know the Chemical Society gathers the wide-flung reviews of these Reports and forwards them to me, no doubt to make sure I read them and for my self-mortification, sometimes on behalf of savaged contributors. It is rewarding to find that most reviewers are constructive and endeavour to help by highlighting parts of the Report they find pleasing or disappointing but, more than that, by suggesting ways to achieve an improved coverage. It goes without saying that I welcome also comments from individuals either verbal or written.

To close, I must express my heartfelt appreciation to the present reporters to Volume 5 for their erudite and well-produced typescripts which were a pleasure to edit. It is somewhat invidious to select individual contributors but three deserve special credit. Firstly, John Bowie gets the gold medal for the first contribution to reach me this year and secondly, the creditor for the wooden spoon shall be nameless but he can stir his chocolate with it. Finally, but not least, Malcolm Rose deserves a special vote of thanks for his painstaking work on assembling the cumulative index. Already, he has opted out of the next one due in 1989!

R. A. W. JOHNSTONE

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## Theory and Energetics

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BY R. A. W. JOHNSTONE

This chapter covers theoretical developments in ion chemistry particularly with regard to application of theory to experimental work and the reflective effect of the latter on the development of theory. The last few years have seen renewed interest in the application of theory to the understanding of ion fragmentation and ion/neutral interactions. Frequently, developments in one area of mass spectrometry have spread over into others so that, although this chapter is divided into sections, extensive cross-references to other sections have had to be made to achieve overall coverage. For this reason, the division into sections has a strong flavour of convenience rather than strict logic but it is hoped the subject matter is more readily digestible and comprehensible treated this way. Photoelectron photoion coincidence spectroscopy is covered by the special review in Chapter 3 and is not dealt with as such here although results are referred to when necessary. The use of molecular orbital theory in mass spectrometry was comprehensively reviewed in Volume 4 of this series and, using criteria developed there, only the more significant applications and developments since then are reviewed in this Chapter.

### 1 Thermochemical Aspects

By well-known energy cycles, thermochemical data, such as heat of reaction and heat of formation, are interdependent in that one can be derived from others. Therefore, the division of this section into sub-sections describing for example, heats of formation, electron affinities, and proton affinities separately is artificial but has been done for convenience in dealing with the literature and for emphasizing particular points of interest.

A valuable compilation of thermochemical data for gaseous ions has appeared<sup>1</sup> and a review on studies of metastable ions which lists advantages of their use as ions of low internal energy for determining thermochemical thresholds.<sup>2</sup>

**Free Energies of Reaction.**—Total free energy changes in a reaction ( $\Delta G^\ominus$ ) are dealt with here in discussion of the derivation of heat of reaction ( $\Delta H^\ominus$ ) from equilibrium measurements on ion/molecule reactions. Fragmentation of isolated ions is dealt with in the section on RRKM theory. Free energy and heat of reaction

<sup>1</sup> H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data*, 1977, **6**, Suppl. 1, 783 pp.

<sup>2</sup> R. K. Boyd and J. H. Beynon, *Internat. J. Mass Spectrometry Ion Phys.*, 1977, **23**, 163.

are linked through the equation,  $\Delta G^\ominus = \Delta H^\ominus - T \Delta S^\ominus$ , where  $T$  is temperature and  $\Delta S^\ominus$  the change in entropy. Also,  $-\Delta G^\ominus = RT \ln K$ , in which  $K$  is the equilibrium constant for reaction. Usually,  $\Delta S^\ominus$  is very small and put equal to zero so that,  $-\Delta G^\ominus \cong \Delta H^\ominus$ . An empirical correlation of exothermicity and activation energy is discussed later.<sup>3</sup>

Equilibrium constants determined from ion/molecule reactions may be in error through competitive reaction, differential ion losses, or slow arrival at equilibrium. Suitable methods and precautions for obtaining equilibrium constants from measurements in ICR cells have been discussed.<sup>4</sup> A further source of error is the extraction and trapping fields in many types of apparatus which give a non-Maxwell-Boltzmann distribution to the ions, *i.e.* the ions have an effective temperature greater than ambient. This point is discussed further for ICR and SIFT techniques in the section on ion/molecule reaction and for ion mobilities in the section of that name. After emphasizing this possible error, a satisfactory way of removing it from time-resolved experiments has been described.<sup>5</sup> Equilibrium constants are measured for different values of the ratio,  $E/P$ , in which  $E$  is the strength of the electric extraction field and  $P$ , the pressure of gas in the apparatus. The value of  $K$  and therefore  $\Delta G^\ominus$  is obtained by extrapolation to  $E/P$  equal zero; this technique provided a heat of reaction for  $\text{CO}_2\text{H}^+(\text{CH}_4, \text{CO}_2)/\text{CH}_5^+$  in excellent agreement with other work using the flowing afterglow and ICR methods.

The common practice of putting  $\Delta S^\ominus = 0$  for ion/molecule reactions has been examined and found satisfactory.<sup>6</sup> Using the unimolecular reaction rate equation,  $K = ZP \exp(E/RT)$ , and making one or two assumptions, these authors showed that  $\Delta S^\ominus$  could be estimated through the expression,  $\Delta S^\ominus = R \ln(Z_f/Z_p)$ , where  $Z_f$ ,  $Z_p$  are the collision rate constants for forward and back reactions; these collision rate constants can be calculated (see section on ion/molecule reactions). Estimates of  $\Delta S^\ominus$  for a number of reactions were shown to be small, of the right order of magnitude, and in the right direction.

Failure to ensure ions have been thermalized, *i.e.* have internal and kinetic energies corresponding to ambient temperatures, is a cause for concern when determining thermochemical quantities from equilibrium measurements. It has been shown that, at least for  $\text{H}^+$ -transfer, the reaction,  $\text{BH}^+ + \text{B} \rightleftharpoons [\text{BHB}^+]* \rightleftharpoons \text{B} + \text{BH}^+$ , is so efficient that the  $\text{BH}^+$  ions are rapidly relaxed.<sup>7</sup>

The sign of  $\Delta H^\ominus$  can be inferred in ICR experiments from the variation of the double-resonance signal with variation in the irradiating field strength.<sup>8</sup> Thus, by use of bracketing reactions, upper and lower limits can be set for  $\Delta H^\ominus$ ; this point is illustrated in the later section on proton affinities.

All of these thermochemical quantities are determined in the dilute gas-phase in which there are no solvent effects (heat of solvation, dielectric, viscosity, and so

<sup>3</sup> M. Meot-Ner and F. H. Field, *J. Amer. Chem. Soc.*, 1978, **100**, 1356.

<sup>4</sup> W. R. Davidson, M. T. Bowers, T. Su, and D. H. Aue, *Internat. J. Mass Spectrometry Ion Phys.*, 1977, **24**, 83.

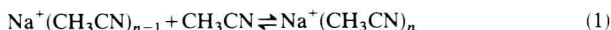
<sup>5</sup> G. G. Meisels, R. K. Mitchum, and J. P. Freeman, *J. Chem. Phys.*, 1976, **80**, 2845.

<sup>6</sup> S. G. Lias and P. Ausloos, *J. Amer. Chem. Soc.*, 1977, **99**, 4831.

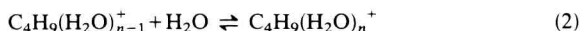
<sup>7</sup> T. B. McMahon and J. L. Beauchamp, *J. Phys. Chem.*, 1977, **81**, 593.

<sup>8</sup> T. A. Lehman and M. M. Bursey, 'Ion Cyclotron Resonance', Wiley, New York, 1976.

on). However, solvent can greatly influence both the extent and nature of a reaction, with products changing and also rates by orders of magnitude from the gas-phase reaction. Further, ionic reactions in solution always have a gegenion which itself can modify the reaction. Bridging the gap between gas-phase and solution-phase has been attempted with considerable success. For example, the interaction of clusters of  $\text{CH}_3\text{CN}$  molecules with  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , or  $\text{Cs}^+$  has been examined, with  $\Delta G^\ominus$ ,  $\Delta H^\ominus$ , and  $\Delta S^\ominus$  measured for such as reaction (1).<sup>9</sup>



Calculations based on simple electrostatics indicate that the weak interaction of a single  $\text{CH}_3\text{CN}$  molecule with a negative ion is due to the diffuse distribution of the positive end of its dipole over the carbon and hydrogen atoms. In contrast, the negative pole of the dipole, strongly localized on nitrogen, leads to strong interaction with a positive ion. Comparison of reaction (1) with a similar one for negative ions, shows that at  $n=5$ , the overall interaction with negative ions becomes slightly more favourable. In a similar piece of work, the differences between the stabilities of complexes of  $\text{K}^+$  ions with nitrogen and oxygen bases were found to be very much smaller than the differences in the proton affinities of these bases.<sup>10</sup> The exothermicity of hydration of  $\text{C}_4\text{H}_9^+$  ions (2) changes as the number of solvent molecules increases. For  $n=1$ , the exothermicity was significantly lower than the values for  $n=2, 3$ .<sup>11</sup> The stability of the  $\text{NO}^+\text{N}_2$  ion cluster has been examined<sup>12</sup> from 178 to 273 K, giving  $\Delta H^\ominus$ ,  $\Delta S^\ominus$  values and a bond-dissociation energy,  $D_0(\text{NO}^+-\text{N}_2) = 4.98 \pm 0.12 \text{ kcal mol}^{-1}$ .



**Electron Affinities.**—Negative ion mass spectrometry has received considerably increased interest in the past few years, prompting the appearance of an extensive review<sup>13</sup> and the issue of a third edition of a classic text-book on the subject.<sup>14</sup> Because of this increased interest, it was thought opportune to discuss somewhat more fully than usual some of the more exciting advances in this area. As many of the techniques used in negative ion chemistry are similar to or identical to those used in positive ion chemistry, their fuller description in this section automatically implies less description in other later sections of this Chapter concerned with positive ions.

The simple reaction (3) requires an enthalpy of reaction equal to the difference in heats of formation of the negative ion ( $\text{AB}^-$ ) and the neutral ( $\text{AB}$  atom, radical, or molecule). This enthalpy, the electron affinity (EA), cannot be determined by direct electron attachment or exothermic electron transfer.



<sup>9</sup> W. R. Davidson and P. Kebarle, *J. Amer. Chem. Soc.*, 1976, **98**, 6125.

<sup>10</sup> W. R. Davidson and P. Kebarle, *J. Amer. Chem. Soc.*, 1976, **98**, 6133.

<sup>11</sup> K. Hiraoka and P. Kebarle, *J. Amer. Chem. Soc.*, 1977, **99**, 360.

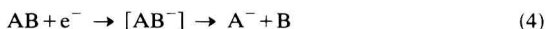
<sup>12</sup> D. L. Turner and D. C. Conway, *J. Chem. Phys.*, 1976, **65**, 3944.

<sup>13</sup> J. G. Dillard, *Chem. Rev.*, 1973, **73**, 589.

<sup>14</sup> H. S. W. Massey, 'Negative Ions', Cambridge University Press, London, 1976.



For the particularly stable radical,  $(\text{CF}_3)_2\text{NO}^\bullet$ , the corresponding negative ions were found to be about forty times longer lived than similar ions with similar numbers of degrees of freedom.<sup>15</sup> This relative stability of a negative ion formed by direct electron attachment was ascribed to completion of pairing of electrons in the molecular orbitals of the radical; SCF molecular orbital calculations supported this hypothesis. Attachment began at 0 eV and exhibited a maximum at  $1.2 \pm 0.1$  eV. Some limits to electron affinities were set by observed dissociative attachment reactions of  $(\text{CF}_3)_2\text{NO}^\bullet$ . Reaction of a slow electron with a neutral (AB) frequency leads to dissociative resonance electron capture, whereby the electron is deposited in an anti-bonding molecular orbital, weakening bonds sufficiently and depositing sufficient energy to cause the ion to fragment as shown in reaction (4). Dissociative electron capture affords the basis of one method for determining electron affinities as in determination of these values for  $\text{NaBO}_2$  and  $\text{KBO}_2$  formed by electron ionization of complexes,  $\text{M}_2\text{BO}_2\text{F}$  ( $\text{M} = \text{Na}, \text{K}, \text{Cs}$ ), present in the vapour phase of mixtures of MF and  $\text{MBO}_2$ .<sup>16</sup> The other main methods used in mass spectrometry include the (usually) very accurate photo-detachment of electrons from negative ions, emission of negative ions from surfaces bombarded with beams of neutral or charged species, charge-exchange between charged and uncharged species, and estimation of electron affinities from other measured thermochemical data or from *ab initio* molecular calculations.



Most *ab initio* molecular orbital calculations yield eigenvalues ( $\epsilon$ ) giving not only the energies of orbitals occupied by electrons but also the virtual energies of unoccupied or 'ghost' orbitals. By assuming no electron correlation or relaxation effects<sup>17</sup> (Koopmans' theorem) on addition of an electron to the lowest unoccupied molecular orbital (LUMO), its eigenvalue may be equated to the electron affinity. Recently, such calculations have been carried out on simple molecules and led to an unexpected but simple relationship between electron affinity and permanent dipole moment:  $\text{EA (calculated)} = -\epsilon(\text{LUMO}) = 0.562 + 0.129\mu$  (calculated), where the electron affinity is expressed in electron-volts and the dipole moment,  $\mu$ , in Debyes.<sup>18,19</sup> Advanced molecular orbital calculations with correct choice of basis sets yield values of dipole moments close to those observed experimentally and this relationship can be used to predict electron affinities from dipole moments or *vice versa*, although it appears to be valid only in the interval,  $5 < \mu, < 10 \text{ D}$ , and not so when  $\mu \leq (\text{ca}) 4.4 \text{ D}$ .<sup>19</sup> The correlation applies only to simple polar molecules like LiH and it would be useful to know whether or not a similar correlation holds for larger molecules with smaller dipole moments. These calculations have shown further that, barring exothermic dissociative electron attachment, all electronically non-degenerate polar molecules with  $\mu > 1.625 \text{ D}$  will have positive electron affinities if the calculated Born-Oppenheimer

<sup>15</sup> P. W. Harland, *Internat. J. Mass Spectrometry Ion Phys.*, 1977, **25**, 61.

<sup>16</sup> V. E. Shevchenko, M. K. Iljin, O. T. Nikitin, and L. N. Sidorov, *Internat. J. Mass Spectrometry Ion Phys.*, 1976, **21**, 279.

<sup>17</sup> For a full discussion of molecular orbital theory in mass spectrometry see, B. N. McMaster in this series, Volume 4, ed., R. A. W. Johnstone, London Chemical Society, 1977, pp. 1-9.

<sup>18</sup> K. D. Jordan, *J. Chem. Phys.*, 1976, **65**, 1215.

<sup>19</sup> K. D. Jordan, *J. Chem. Phys.*, 1977, **66**, 3305.