Ionization Potentials of Aromatic Molecules Determined by Analytical Interpretation of Electron Impact Data

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The analytical technique proposed by Morrison [1] has been tested on ionization efficiency curves obtained using an unmodified mass spectrometer. Ionization potentials of a series of aromatic amines have been found by this method and have been used to determine the best parameters for use in calculations by the Streitwieser ω-technique.

The ionization potential of a molecule can be determined by measuring its ionization efficiency curve using a mass spectrometer with an electron impact source and comparing the position of this curve on the energy scale with that of the ionization efficiency curve of a molecule of known ionization potential. Because of the energy distribution of electrons derived from a hot filament the observed curves differ from true ionization efficiency curves, and reliable ionization potentials can only be obtained if the true curves of sample and standard have the same shapes. Recent work has shown this is seldom the case and for this reason the electron impact method is less reliable than, for example, molecular photoelectron spectroscopy [2]. A technique which involves mass analysis and in which a wide range of energies can be covered is essential, however, for the determination of appearance potentials of fragment ions and multiply charged ions. It is therefore important to find a less arbitrary method of determining ionization and appearance potentials from electron impact data.

Morrison [1] has proposed a method whereby the energy resolution of experimental ionization efficiency curves can be improved by analytical reduction of the energy spread. In the present work this method has been tested on data for unfragmented molecules using a conventional mass spectrometer. The results show a considerable improvement over those obtained by application of the usual extrapolation procedures, such as that of Lossing, Tickner, and Bryce [3].

Experimental

The mass spectrometer used was a double-focussing instrument similar to that described by Craig and Errock [4]. The ionizing electron beam was derived from a tungsten filament and was collimated by an axial field of about 200 gauss. The precise measurement of the electron accelerating voltage in a source some 4 kV above earth has, in the past, presented some difficulty. In the present work it was found possible to operate a solid-state digital voltmeter (Roband, type RDV 4) at the source potential, the voltmeter being suitably insulated and its mains supply taken from an isolating transformer. This method provides continuous and precise measurement of the accelerating voltage. First derivative ionization efficiency curves were obtained by changing the accelerating voltage in steps of exactly 0.1 volt and recording the resulting changes of ion beam intensity. This method shows an advantage over the arithmetical treatment of the direct curves. The accuracy is lowest in the higher voltage regions of the curve where the change in intensity for unit change in electron energy is only a small fraction of the total beam current. At the lowest ion currents the accuracy is limited by random noise. Because of contact potentials the energy given to the electrons is not necessarily equal to the applied voltage and the energy scale was established in the usual way by reference to the known ionization potentials of standard substances. Measurements were repeated so that drifts in the energy scale could be detected. The largest changes observed were about 0.1 eV, but in most cases no change was found.

The analytical method requires a knowledge of the energy distribution of the electrons. This was derived from the reversed second differential ionization efficiency curve for helium [5]. The observed half-height width was 0.8 to 1.0 eV and there was a small tail on the low energy side. This distribution is typical of normal mass spectrometer sources.

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Calculation

If the fraction of the electrons having thermal energies between U and $U + \Delta U$ is designated $m(U)$ and the electron accelerating voltage is V, the observed ionization efficiency curve can be written:

$$i(V) = \int I(V+U)\, m(U)\, \mathrm{d}U$$

where $I(V+U)$ is the true ionization efficiency. Two methods are available for solving this equation in the case of sampled functions; the iterative unfolding procedure of Burger and van Cittert [6] and the Fourier transform method [7]. The experimental data must first be smoothed and Morrison's iterative smoothing process [1] has proved very effective. Computer programmes have been written for smoothing the data by this method and for unfolding by each of the techniques mentioned above. The programmes were tested on artificial data and also by unfolding experimental curves for helium. The result of one such test is shown in Fig. 1 in which it can be seen that the energy resolution has been improved by a factor of about two. The increase in resolution is limited by noise in the data and by inaccuracy in the measured electron energy distribution.

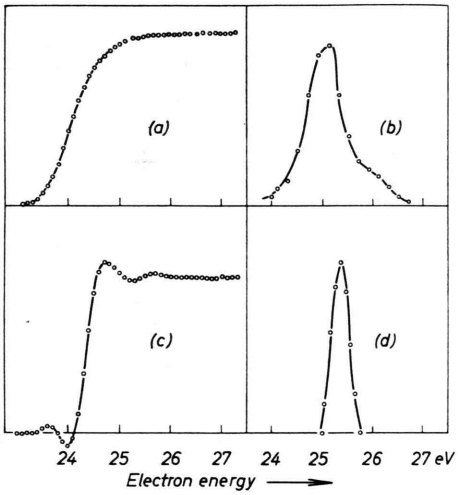

Fig. 1. Ionization efficiency data for helium. (a) Smoothed experimental curve. (b) Second derivative from (a). (c) Result of unfolding (a) in terms of (b) by the Fourier transform method. (d) Second derivative from (c).

The iterative method requires less computer time than the Fourier transform method, and it is easier to incorporate the condition that the true curve $I(U+V)$ is never negative into it. Residual errors appear as short period noise in the solutions, strongest in the high energy region. The Fourier transform procedure, on the other hand, gives smooth curves in which residual errors of the data produce long period oscillations.

Results

Tests of these methods of reducing the effects of the energy spread of the electrons were made using simple substances whose ionization potentials are well known, and for which good results could also be obtained by extrapolation methods. The results are given in Table 1, and the effect of the smoothing and unfolding procedures on a typical curve are shown in Fig. 2. Table 1 also contains the results obtained from the same data by the extrapolation method: the ionization potentials obtained by both methods of interpretation agree well with the accepted values.

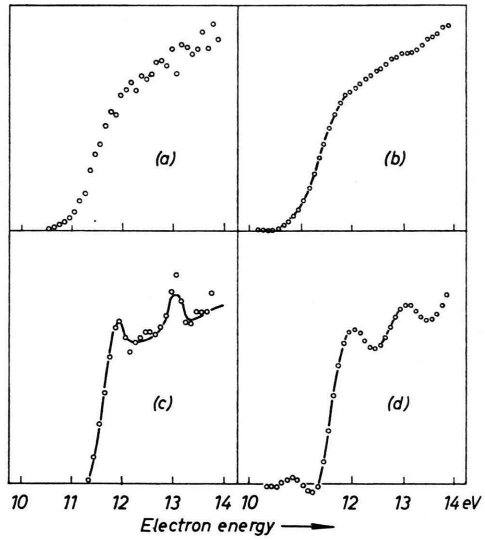

Fig. 2. Ionization efficiency data for acetylene. (a) Experimental points. (b) Result of computer smoothing of (a). (c) Result of unfolding (b) by the Burger and van Cittert method. (d) Result of unfolding (b) by the Fourier transform method.

Application of extrapolation procedures to electron impact data for aromatic compounds often leads to ionization potentials which are too high by several tenths of an electron volt. This is because ionization

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Compounds	Calculation *	Ionization Potential Differences		
		Analytical	Extrapolation	Literature
$Xe-C_2H_2$	B. v. C.	0.67 ± 0.10	0.69 ± 0.05	0.73[8,9]
$Xe-C_2H_2$	F. T.	0.70 ± 0.05	0.65 ± 0.10	0.73[8,9]
$CO-C_2H_2$	B. v. C.	2.60 ± 0.15	2.53 ± 0.10	2.61[10,9]
$C_2H_2-C_2H_5OH$	B. v. C.	1.00 ± 0.10	0.90 ± 0.05	0.92[9,11]
A–Kr	B. v. C.	1.62 ± 0.1	1.68 ± 0.05	1.76[8]
Kr–Xe	B. v. C.	1.89 ± 0.1	1.82 ± 0.05	1.87[8]
Xe–Aniline	B. v. C.	4.28 ± 0.1	4.00 ± 0.1	4.29[8,12]
Xe–Benzene	B. v. C.	2.79 ± 0.1	2.50 ± 0.1	2.89[8,9]

* B. v. C. indicates unfolding by the iteration procedure, F. T. unfolding using Fourier transforms.

Table 1. Tests of the analytical method on simple substances.

at the threshold has a low probability and is overshadowed by more probable processes occurring at higher energies[13]. Aromatic compounds provide, therefore, a more stringent test of the analytical interpretation of ionization efficiency data. The results of preliminary tests on benzene and aniline are shown in Table 1; these values are closer to the accepted ionization potentials than are those obtained by conventional electron impact methods. Application of the Fourier transform programme to the experimental curves gave less satisfactory results; oscillations near the origin obscured the first steps in the inverse transforms.

To provide a more extensive test of the method more accurate experimental data for five aromatic hydyrocarbons were obtained. This was achieved by measuring the shapes and relative positions of the ionization efficiency curves in separate experiments. Drifts of the energy scale were found to be small when only one substance was present, and this made it possible for extended measurements to be carried out with a valuable increase in accuracy. The relative positions of the curves were determined in experiments on mixed gases which were made rapidly to minimise the effects of drifts. Each hydrocarbon was compared with two standards, acetylene and xenon to compensate for the added uncertainty caused by fitting the curves; the difference between the ionization potentials of the two standard gases was also redetermined. Since more than sufficient information to fix the positions of the curves was available the best positions were found by a least-squares treatment.

When the curves were unfolded in terms of the energy distribution by the two mathematical methods almost identical smooth curves were obtained. The first ionization potentials derived from these curves are shown in Table 2, which also shows the results of interpreting the same experimental data by an extrapolation method. In the cases of benzene, naphthalene and biphenyl the agreement with accepted values has been improved considerably by the analytical treatment. For azulene a discrepancy of 0.3 eV still remains, and for biphenylene no previous measurement has been reported. The apparent ionization potentials of these two compounds have not been reduced by the analytical treatment, so it is possible that finer energy resolution is necessary in these cases.

Compound	Analytical	Extra- polation	Litera- ture
Benzene	9.21 ± 0.2	9.71 ± 0.05	9.24[9]
Naphthalene	8.24 ± 0.15	8.49 ± 0.05	8.12[12]
Azulene	7.76 ± 0.15	7.82 ± 0.05	7.43[14]
Biphenyl	8.22 ± 0.15	8.72 ± 0.06	8.27[15]
Biphenylene	7.95 ± 0.15	8.00 ± 0.06	—

Table 2. First ionization potentials of aromatic hydrocarbons.

Aromatic Amines

The agreement between the results of the two mathematical unfolding procedures for the aromatic hydrocarbons provides some justification for the use of the simpler iterative method. This method was applied to the ionization efficiency curves of a series of aromatic amines, for which published electron im-

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Compound	Analytical, this work	Previous electron impact	Charge transfer	Calculated
Aniline	7.84 ± 0.1	8.23[16]	7.76[18]–7.95[19]	7.84
o-Toluidine	7.68 ± 0.1	8.38[17]	7.75[19]	7.65
m-Toluidine	7.57 ± 0.1	8.27[17]	7.75[19]	7.73
p-Toluidine	7.60 ± 0.1	8.14[17]	7.65[19]	7.63
N-Methylaniline	7.65 ± 0.1		7.58[18], 7.60[19]	7.71
N:N-Dimethylaniline	7.30 ± 0.1		7.44[18], 7.30[19]	7.56
N-Methyl o-toluidine	7.58 ± 0.1			7.52
N-Methyl m-toluidine	7.45 ± 0.1			7.60
N-Methyl p-toluidine	7.58 ± 0.1			7.50
Benzylamine	9.04 ± 0.1			8.92
N-Methyl N-benzylaniline	7.44 ± 0.1			7.45

Table 3. Aromatic amines.

pact ionization potentials are almost invariably higher than values obtained by charge transfer absorption measurements. The original experimental procedure used in the test of the method on simple compounds was employed. The first ionization potentials obtained are shown together with the results of other determinations in Table 3. They are in better agreement with charge transfer absorption results than are other electron impact values.

Calculation of the Ionization Potentials of Aromatic Amines

Streitwieser [20] has used the Wheland–Mann or ω-technique to calculate the ionization potentials of some amines and chose values of the variable parameters that give agreement with previous electron impact results. We have derived a set of parameters which reproduce our measured values of the amine ionization potentials when used in ω-technique calculations.

In the ω-technique the π-electron energy of the neutral molecule is first calculated by the simple Hückel method using the expressions:

$$\alpha_r = \alpha_0 + h_r \beta_0$$
$$\beta_{rs} = k_{rs} \beta_0$$

for the α- and β-integrals for heteroatoms. Methyl groups are treated as heteroatoms in hyperconjugation with the aromatic system and are assigned h and k values. It is assumed that the ion is formed by removal of an electron from the highest occupied molecular orbital; charge densities on each atom are then calculated from the coefficients of the atomic orbitals of the neutral molecule. These charge densities q_r are used to modify the α-values of the atoms in the ions by means of the equation:

$$\Delta\alpha_r = \omega (n_r - q_r) \beta_0$$

where n_r is the number of electrons contributed to the π-system by atom r, and ω is a parameter normally given the value of 1.4. The secular matrix for the ion is diagonalised using the new α-values, and the π-energy of the cation is obtained from the resulting eigenvalues. The cation energy can be refined by further iterations, but this has not been found necessary. The ionization potential is obtained by subtracting the calculated energy of the neutral molecule from that of the cation.

In our calculations the values of α_0, β_0 and ω were those given by Streitwieser [20], and the h and k parameters were varied to find the best fit with the experimental results. The values finally chosen were as follows: h_{N} 1.7, k_{CN} 1.2, k_{Me} 3.0, $k_{\mathrm{C-Me}}$ 0.7, $k_{\mathrm{N-Me}}$ 0.5. The calculated ionization potentials are shown in Table 3. In order to reproduce our aniline ionization potential of 7.84 eV we use the parameter values $h_{\mathrm{N}} = 1.7$ and $k_{\mathrm{CN}} = 1.2$. This value for k_{CN} is much higher than the one used by Streitwieser to reproduce the previous electron impact ionization potential, and it is supported by some recent S.C.F. calculations on aniline [21].

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Conclusions

A worthwhile improvement in electron impact ionization efficiency data from an unmodified mass spectrometer can certainly be attained by MORRISON's analytical method of interpretation. An iterative procedure is the simplest mathematical method and is also the most efficient unless the experimental data are unusually accurate. Application of this method to data for aromatic amines has given ionization potentials in agreement with those found in charge transfer absorption studies. Parameters which will reproduce these ionization potentials when used in WHELAND–MANN technique calculations have been derived.

Die Isotopenbeweglichkeiten und deren Temperaturabhängigkeit in geschmolzenem KCl, RbCl und RbBr

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Die kationischen und anionischen Masseneffekte der Beweglichkeiten $\mu_+ \equiv \partial \ln b_{\mathrm{p}-} / \partial \ln m_{\mathrm{p}}$ und $\mu_- \equiv \partial \ln b_{\mathrm{n}+} / \partial \ln m_{\mathrm{n}}$ sowie deren Abhängigkeit von der absoluten Temperatur T wurden bestimmt zu

		μ_+	$\dfrac{\partial \ln \mu_+}{\partial \ln T}$	μ_-	$\dfrac{\partial \ln \mu_-}{\partial \ln T}$
KCl	850 °C	−0,074	1,22	−0,061	0,00
RbCl	825 °C	−0,052	1,13	−0,113	1,39
RbBr	800 °C	−0,073	0,50	−0,115	0,16

Es zeigt sich, daß bei den drei Salzen nicht nur die Masseneffekte $\mu_{\pm}$, sondern in drei von vier prüfbaren Fällen auch die reduzierten Masseneffekte $\mu_{\pm}^{\bullet} = \mu_{\pm} / (z_{\pm} \, D_{\pm} \, F^2/R\,T\,\Lambda)$ mit der Temperatur ansteigen. Dies weist auf ein Kleinerwerden der ladungstragenden zusammengesetzten Bewegungseinheiten mit steigender Temperatur hin.

Die Alkalihalogenide sind die typischsten Salze, und deshalb ist die Kenntnis der Transporteigenschaften ihrer Schmelzen für das allgemeine Verständnis der Transportphänomene in Salzschmelzen grundlegend. Was die Isotopieabhängigkeit der Ionenbeweglichkeiten in Alkalihalogenidschmelzen betrifft, so kennt man diese bisher nur für die Lithiumisotope [1, 2]. In der vorliegenden Arbeit werden nun die Isotopieeffekte der Kationen- und Anionenbeweglichkeiten in geschmolzenem KCl, RbCl und RbBr einschließlich ihrer Temperaturabhängigkeiten mitgeteilt. Bei dem einzigen bisher auf die Temperaturabhängigkeit hin untersuchten Halogenid, dem TlCl, sind die Temperaturkoeffizienten beider Isotopieeffekte negativ [3, 4]. Dagegen zeigen die hier untersuchten Alkalihalogenide positive Temperaturkoeffizienten. Diese Befunde werden am Schluß der Arbeit unter Zuhilfenahme von Vergleichen mit dem Verhalten von Ionengasen und Ionenkristallen diskutiert.

Experimentelles

Die Isotopieeffekte der Kationenbeweglichkeiten wurden aus anodenseitigen Anreicherungen der schweren Kationen bei der Elektrolyse der Salze in üblicher Weise [5] bestimmt, wobei eventuell vom anodisch entwickelten Halogengas mitgerissene Salzdämpfe in einer mit flüssiger Luft beschickten Falle abgefangen und mit analysiert wurden. Die kathodenseitige Metallabscheidung wurde dabei durch Zufuhr von Halogengas verhindert.

Ein entsprechendes Vorgehen für anionische Isotopenanreicherungen, nämlich anodenseitige Metallzufuhr und kathodenseitige Metallabscheidung, war wegen der

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