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Effects of Isotopic Labeling and Molecular Structure on Probability of Ionization by Electron Impact

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Isotope effects have been reported on probability of ionization of molecules by photons, by excited rare-gas atoms, and by beta rays. Such effects furnish evidence that ionization occurs largely as a secondary process in competition with nonionizing processes following primary excitation to an energy level above the ionization potential. Measurements of total ion current produced in a mass-spectrometer source show similar effects for the case of ionization by 70-V electrons. Experimental support has been obtained also for the corollary that probability of ionization depends upon molecular structure and is not simply, as has been postulated, a constitutive property of the atoms.

COMPELLING evidence¹⁻⁵ indicates that ionization of molecules either by photon impact or by collision with excited rare-gas atoms is in large part a secondary process. Primary excitation to an energy level above the ionization potential is followed after elapse of a finite period of time by either pre-ionization or competing nonionizing events grouped together loosely as "dissociation." Anomalous results in an attempted isotopic analysis of deuterated ethanal in the mass spectrometer could stem from isotope effects arising out of such competition⁶; this possibility prompted us to seek evidence for a similar sequence of events initiated by electron impact. While the present work was in progress, we learned that differences of 0.6% to 1.3% have now been detected in the probability of ionizing ordinary vs fully deuterated methane, ethene, ethane, and hydrogen by beta rays of about 3 and 18 keV.⁷ Such effects—paralleling those found for the case of collision with an excited rare-gas atom^{2,4}—imply that, for electron impact also, nonionizing reaction paths involving relative motion of atomic nuclei compete effectively with paths leading to ionization.

Isotope effects on probability of ionization by electrons of the comparatively low energies normally used in mass spectrometry are expected to be greater than for beta rays.^{4,8} The consequence of such effects is clear with regard to the usual assumption for isotopic analysis^{9,10} that ionization probability is equal for all isotopic species of a molecule. Furthermore, competition between ionization and dissociation, to which such effects are attributed, is incompatible with the widely accepted view that cross section for ionization of gaseous molecules by impact of 50-to-100-V electrons de-

pends solely on the number and kind of atoms in the molecule and is independent of structure.¹¹

We have measured total ion current produced by 70-V electrons in benzene unlabeled, -1,3,5-*d*₃, and -*d*₆; toluene unlabeled, - α -*d*₃, -ring-*d*₆, and -*d*₈; and phenanthrene unlabeled and -*d*₁₀. To test specifically for effects of molecular structure, we have included also two sets of isomeric hydrocarbons: *n*-octane, 2,2,4-trimethylpentane, and 2,3,3-trimethylpentane; and *n*-dodecylbenzene and 1,3,5-tri(*sec*-butyl)benzene.

EXPERIMENTAL

Measurements were made with a modified¹² Consolidated Model 21-103 mass spectrometer, equipped with a vacuum lock for sample admission. The sample is loaded by capillary action into a length of 0.010-in.-i.d. indium tubing, which is then cut to a standard length and sealed in a single operation.¹³ The tube, containing about 0.6 μ l of the sample, is admitted via the vacuum lock to a glass expansion chamber heated to 250°. The indium melts within a few seconds, permitting the sample to vaporize and to enter the ionization chamber.

The ion repellers are maintained at a fixed negative potential of about 3.2 V, and total ion current is measured between the repellers and the source chamber. The arrangement is similar to those described elsewhere,^{11,14,15} except that variation of the negative potential with ion current is eliminated by using a null current-measuring circuit. Small variations in sample size are probably the major cause of scatter in total-ion-current measurements.

Benzene-*d*₆ and toluene- α -*d*₃ were purchased from Merck of Canada. We are indebted to M. J. S. Dewar,

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TABLE I. Total ion currents.

Compound	Total ion current, (arbitrary units) ^a	Relative values
Benzene unlabeled	422±3	1.00
-1,3,5- <i>d</i> ₃	427±3	1.01
- <i>d</i> ₆	436±3	1.03
Toluene unlabeled	426±5	1.00
- <i>α-d</i> ₃	429±3	1.01
-ring- <i>d</i> ₅	428±4	1.01
- <i>d</i> ₈	442±4	1.04
Phenanthrene unlabeled	531±2	1.00
- <i>d</i> ₁₀	552±4	1.04
<i>n</i> -Octane	421±2	1.00
2,2,4-Trimethylpentane	391±4	0.93
2,3,3-Trimethylpentane	397±4	0.94
<i>n</i> -Dodecylbenzene	437±5	1.00
1,3,5-Tri(<i>sec</i> -butyl)benzene	432±4	0.99

^a For a standard liquid volume of sample.

of the University of Chicago, for the gift of the benzene-1,3,5-*d*₃; to F. R. Jensen, of the University of California, for the toluene-ring-*d*₅; and to L. C. Leitch, of the National Research Council of Canada, for the phenanthrene-*d*₁₀. Isotopic purities of all labeled materials, estimated by low-voltage mass spectrometry,¹⁶ were about 95%.

RESULTS AND DISCUSSION

Results are summarized in Table I. Each reported value is the average of three to nine measurements following separate sample admissions; the uncertainties shown are average deviations. Total ion currents of all deuterated species are greater than those of the corresponding unlabeled species. The increases found in partly deuterated species are less than the combined limits of error, but those in fully deuterated species are greater and almost certainly are real. Similarly, total ion currents of the isomeric arenes are equal within the combined limits of error. But the greater difference among total ion currents of the isomeric octanes leaves little doubt that molecular structure can influence ionization cross section. Moreover, in the octanes as well as in the labeled species, the direction of the difference is that to be expected in terms of the model under consideration. The several weak bonds in 2,2,4- and 2,3,3-trimethylpentanes, as contrasted to *n*-octane, would promote dissociation in competition

with ionization of the initially formed superexcited molecules.

The effects observed may be due in part to differences in liquid molar volume. Such differences can be taken into account by dividing total ion current by density/molecular weight. Densities of the unlabeled materials¹⁷ and of benzene-*d*₆¹⁸ are available. If such a correction is made, the difference in total ion current between benzene unlabeled and -*d*₆ is reduced from 3% to 2.7%; that between *n*-octane and 2,2,4-trimethylpentane is reduced from 7% to 6%; and that between *n*-octane and 2,3,3-trimethylpentane is *increased* from 6% to 9%.

The hypothesis that molecular ionization cross section is a constitutive property of the atoms is the basis for the total-ionization method of standardizing mass-spectral sensitivities; this has been incorporated in calculating procedures for type analysis of complex hydrocarbon mixtures.^{19,20} That such calculating procedures are satisfactory may be in part a delusion; reliable alternative methods of analyzing such materials are nonexistent. On the other hand, dissociation seems to compete most effectively with pre-ionization at energy levels within a few electron volts of the ionization potential²⁻⁴; at higher energies, probability of ionization rapidly approaches 100%.²⁻⁵ Thus, depending on the energy-transfer function for collision with 70-V electrons, effects of structure on ionization probability may be comparatively small for the hydrocarbons comprising such mixtures.

The results obtained with 70-V electrons confirm and extend the earlier findings^{1-4,7,8} and add emphasis to the implications drawn from them for radiation chemistry. For mass spectrometry, they show clearly that total ionization is not independent of isotopic labeling or of molecular structure. In certain analytical problems, assuming such independence may lead to the best, or even the only, approximation possible at the present state of the art—but nonetheless only an approximation, the quality of which is, in general, unknown.

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