Ion Cyclotron Resonance Study of Ion-molecule Reactions in Benzene: Mechanism of $C_3H_3^+$ Formation

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Ion-molecule reactions in gaseous benzene, benzene-d_6, and their mixtures, particularly the formation process of $C_3H_3^+$, have been investigated using ion cyclotron single- and double-resonance techniques. Double-resonance experiments demonstrated that $C_3H_3^+$ is formed by the ion-molecule reaction: $C_6H_7^+ + C_6H_6 \rightarrow C_3H_3^+ +$neutral product. In C_6H_6–C_6D_6 mixtures, not only $C_3H_3^+$ but also deuterium substituted ions, such as $C_3H_2D^+$ and $C_3HD_2^+$, are formed from $C_6H_7^+$. Quantitative analysis of the double-resonance intensity revealed that $C_3H_3^+$ is formed by the decomposition of the intermediate complex of $[C_6H_7^+–C_6D_6]$, which is a σ-type complex.

Ion-molecule reactions of aromatic hydrocarbons in the gas-phase have been studied using high-pressure mass spectrometry.[2–5] Ions generated from benzene by electron impact are mainly the molecular ion $C_6H_6^+$ and the characteristic fragment ions $C_3H_3^+$, $C_4H_2^+$, $C_4H_3^+$, $C_4H_4^+$, and $C_6H_5^+$.[2–5] It is well known that $C_3H_3^+$ is a stable ion appearing in the mass spectrum of benzene, as well as in a number of hydrocarbon compounds. 2-Propynyl[6] and cyclic[7] structures have previously been proposed as the structure of $C_3H_3^+$, however, at present, $C_3H_3^+$ is considered to be a cyclopropenyl cation.[8] The mechanism of $C_3H_3^+$ formation, however, has not yet been clarified. Ion-molecule reactions in gaseous benzene, especially the mechanism of $C_3H_3^+$ formation, were investigated using ion cyclotron single- and double-resonance (ICSR and ICDR) techniques.[9]

Results and Discussion

Reactions in Benzene. A single-resonance spectrum of benzene obtained at 2×10^{-5} Torr and electron energy of 70 eV is shown in Fig. 1. A number of fragment ions, as well as the molecular ion $C_6H_6^+$, are produced by electron impact on benzene. The spectrum is essentially the same as that obtained by an ordinary mass spectrometer at 1.1×10^{-5} Torr,[2] except for such ions as $C_6H_7^+$, $C_7H_7^+$, $C_8H_7^+$, $C_9H_7^+$, $C_{10}H_7^+$, and $C_{11}H_9^+$. From among the many ions, the present double-resonance study concentrated on $C_3H_3^+$ which is one of the major product inos. Irradiation of $C_6H_7^+$ (*m*/*e* 79) caused on decrease in the intensity of $C_3H_3^+$ (*m*/*e* 39), as is shown in Fig. 2. This double-resonance indicates that $C_3H_3^+$ is not a primary ion produced by electron impact but is a product ion formed by the ion-molecule reaction:

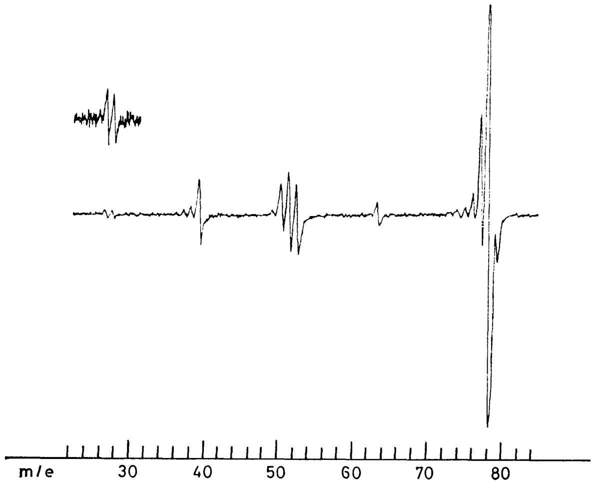


Fig. 1. Single-resonance spectrum of benzene at 2×10^{-5} Torr and 70 eV electron energy. Field modulation yields the derivative presentation.

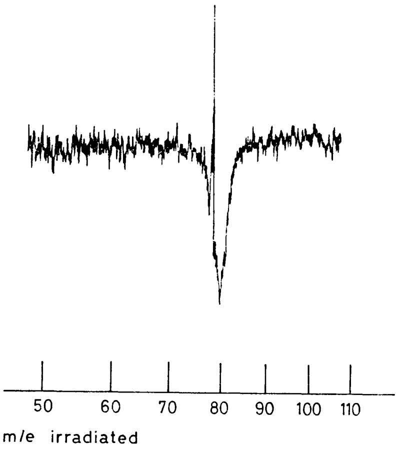


Fig. 2. Double-resonance spectrum of $C_3H_3^+$ in benzene. The sharp spike appearing the frequency (61.4 kHz) corresponding to *m*/*e* 78 is the first sub-harmonic of the observing frequency. This harmonic peak at double the observed ion mass serves as a convenient check on the mass assignment.

$$C_6H_7^+ + C_6H_6 \rightarrow C_3H_3^+ + N, \qquad (1)$$

where N denotes a neutral product. However, the ICDR peak of the precursor ion ($C_6H_6^+$) producing the reactant ion ($C_6H_7^+$) cannot be distinguished by the broadening of the $C_6H_7^+$ peak due to the strong irradiating field (the irradiating field is 4.8 times as strong as the observing field). The ICDR experiment indicates that if the velocity of the reactant ion R^+ is increased by means of irradiating field of resonance frequency at R^+, then a substantial change will occur in the concentration of product ion P^+, when the two ions are coupled chemically in the absence of irradiation. In reaction (1), a change of the $C_6H_7^+$ velocity reduces the abundance of $C_3H_3^+$, and therefore it is concluded that $C_6H_7^+$ should react with C_6H_6 to produce $C_3H_3^+$.

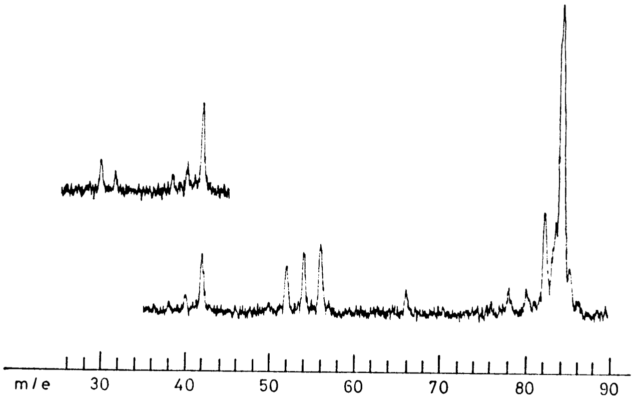


Fig. 3. Single-resonance spectrum of benzene-d_6 at 2×10^{-5} Torr and 70 eV electron energy. Energy modulation yields the absorption presentation.

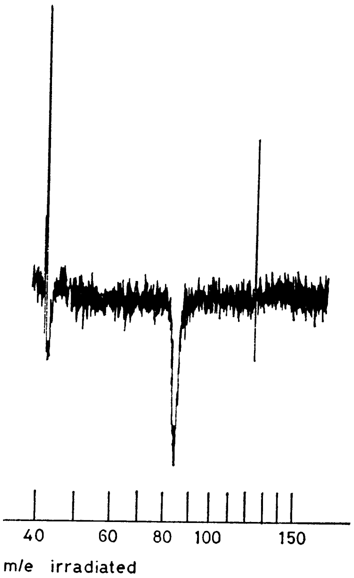


Fig. 4. Double-resonance spectrum of $C_3D_3^+$ in benzene-d_6. The large spike appearing at the frequency (122.8 kHz) corresponding to *m*/*e* 42 results from the interaction of the irradiating and observing oscillators, and the sharp feature at *m*/*e* 126 is due to the irradiaitng oscillator exciting the second subharmonic of the observing frequency.

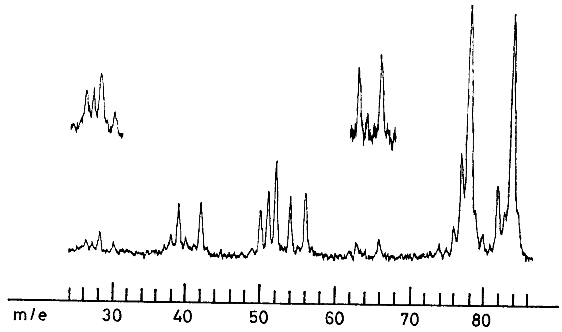


Fig. 5. Single-resonance spectrum of the 1 : 1 mixture of benzene and benzene-d_6 at 2×10^{-5} Torr and 70 eV electron energy.

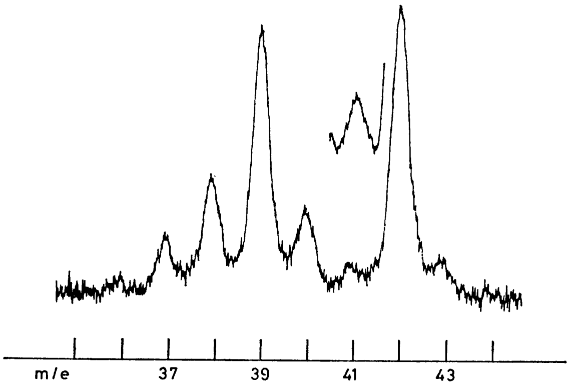


Fig. 6. Single-resonance spectrum recorded with the magnification of the 1 : 1 mixture of benzene and benzene-d_6 at 2×10^{-5} Torr and 70 eV electron energy.

A single-resonance spectrum of benzene-d_6 and a double-resonance spectrum of $C_3D_3^+$ (*m*/*e* 42) are shown in Figs. 3 and 4, respectively. These spectra are the same as those observed in benzene.

Reactions in Benzene and Benzene-d_6 *Mixtures.* Ionic reactions in a mixture of benzene and benzene-d_6 were investigated to clarify the reaction path for $C_3H_3^+$ formation in detail employing single- and double-resonance experiments. Figure 5 shows the single-resonance spectrum of a mixture of benzene and benzene-d_6 (ratio of 1 : 1). In addition to the spectra observed in benzene or benzene-d_6, the new product ions, $C_6HD_2^+$, $C_6H_5D_2^+$, $C_6H_3D_4^+$, and $C_6HD_6^+$, were observed. The single-resonance spectrum recorded with an increase in sensitivity around *m*/*e* 41 is shown in Fig. 6, for which the ions are identified as follows: $C_3H_3^+$ and C_3HD^+ at *m*/*e* 39, $C_3H_2D^+$ and $C_3D_2^+$ at *m*/*e* 40, $C_3HD_2^+$ at *m*/*e* 41 and $C_3D_3^+$ at *m*/*e* 42. The peak at *m*/*e* 41 is uniquely attributable to the ion which contain both hydrogen and deuterium. The formation of this ion suggests that $C_3H_3^+$ is formed not by the direct decomposition of $C_6H_7^+$ or C_6H_6, but by the decomposition of a mixture ion of the benzene and benzene-d_6 molecules.

Double-resonance experiments on a C_6H_6–C_6D_6 mixture (1 : 1 ratio) are shown in Figs. 7 and 8. The irradiation of $C_6H_7^+$ and $C_6D_7^+$ resulted in a decrease in the intensity of $C_3H_3^+$, as is shown in Fig. 7. This ICDR result predicts that the reactant ions which are coupled chemically with the product ion $C_3H_3^+$ are not only $C_6H_7^+$, but also $C_6D_7^+$. The contributions of $C_6H_6D^+$ and $C_6HD_6^+$ to the formation of $C_3H_3^+$ are scarcely observed. Similarly, the irradiation of $C_6H_7^+$ and $C_6D_7^+$ caused a decrease of the intensity of $C_3D_3^+$, as is shown in Fig. 8. The result indicates that the ions reacting with $C_3D_3^+$ are also $C_6H_7^+$ and $C_6D_7^+$. These ICDR results indicate that $C_3H_3^+$ and $C_3D_3^+$ are formed by the following processes:

$$C_6H_7^+ + \left\{\begin{matrix} C_6D_6 \\ C_6H_6 \end{matrix}\right\} \xrightarrow[\text{[}C_{12}H_{13}^+\text{]}]{\text{[}C_{12}H_7D_6^+\text{]}} C_3H_3^+ + N, \tag{2}$$

$$C_6D_7^+ + C_6H_6 \xrightarrow{\text{[}C_{12}H_6D_7^+\text{]}} C_3H_3^+ + N, \tag{3}$$

$$C_6D_7^+ + \left\{\begin{matrix} C_6H_6 \\ C_6D_6 \end{matrix}\right\} \xrightarrow[\text{[}C_{12}D_{13}^+\text{]}]{\text{[}C_{12}H_6D_7^+\text{]}} C_3D_3^+ + N, \tag{4}$$

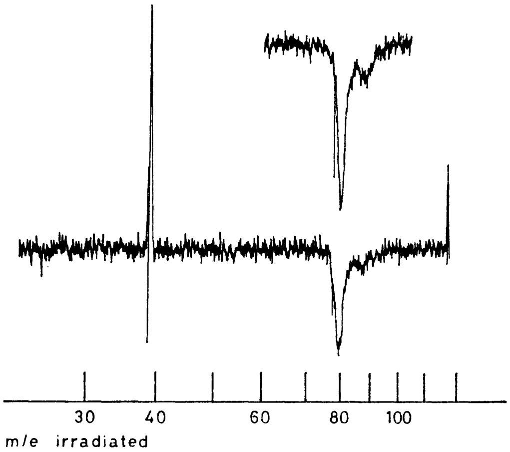


Fig. 7. Double-resonance spectrum of the species at m/e 39 in the 1 : 1 mixture of benzene and benzene-d_6. The large spike appearing at the frequency (122.8 kHz) corresponding to m/e 39 results from interaction of the irradiating and observing oscillators, and the sharp spikes at the frequencies (61 kHz and 41 kHz) corresponding to m/e 78 and m/e 117 are due to the irradiating oscillator exciting the first and second sub-harmonics of the observing frequency, respectively.

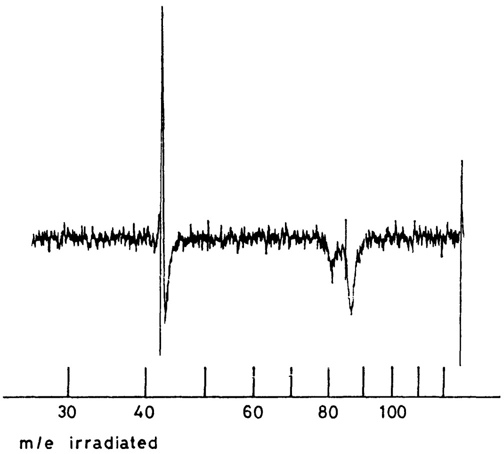
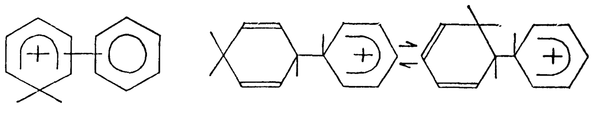


Fig. 8. Double-resonance spectrum of $C_3D_3^+$ in the 1 : 1 mixture of benzene and benzene-d_6. The large spike at m/e 42 results from interaction of the irradiating and observing oscillators, and the sharp spikes at m/e 84 and m/e 126 are due to the irradiating oscillator exciting the first and second overtones of the marginal oscillator, respectively.

$$C_6H_7^+ + C_6D_6 \xrightarrow{[C_{12}H_7D_6^+]} C_3D_3^+ + N. \qquad (5)$$

In order to clarify the structure of the intermediate complex ion $[C_{12}H_{13}^+]$, the intensities of the ICDR peaks were quantitatively examined. The intensity ratio is considered to reflect quantitatively the degree of the contributions of the reactant ions. When the contribution of A ion to the formation of P ion is twice as high as that of B ion, the ICDR spectrum of P should be twice as high at resonance frequency of A than at that of B. Let us assume that the energy dependences of the rate constants for the reactions of $C_3H_3^+$ formation are almost equal, and let us also ignore the isotope effect of hydrogen and deuterium on the $C_3H_3^+$ formation reaction. The ratios of the intensities at the resonant frequencies of $C_6H_7^+$ and $C_6D_7^+$ were found to be $I_{79}/I_{86}=4/1$ and $I_{79}/I_{86}=1/2.7$ for the ICDR spectra of $C_3H_3^+$ and $C_3D_3^+$, respectively. These ratios are not in agreement with the simple ratio of the reactant ion and neutral molecules, which is usually expected for the addition reaction. This means that the ratio directly reflects the decomposition process.

As the intermediate complex for $C_3H_3^+$ formation, it is supposed that there are actually two intermediate complexes, a π-type complex and a σ-type complex:



π-type complex σ-type complex

Here, it is defined that intramolecular exchange exists between H and D in the π-type compex, but does not exist in the σ-type complex. Figure 9 shows the I_{79}/I_{86} ratios of the observed value and the calculated value (see Appendix) in the case of $C_3H_3^+$. Here, I_{79} and I_{86} indicate the ICDR spectral intensities when $C_6H_7^+$ and $C_6D_7^+$ are irradiated, respectively. In the case of the σ-type complex, the I_{79}/I_{86} ratio of the calculated values is in good agreement with that of the observed values. In the case of the π-type complex, however, the calculated ratio does not agree with the observed ratio. This agreement between the observed and calculated ratios is evidence that $C_3H_3^+$ is formed by way of the σ-type complex in the ion-molecule reaction.

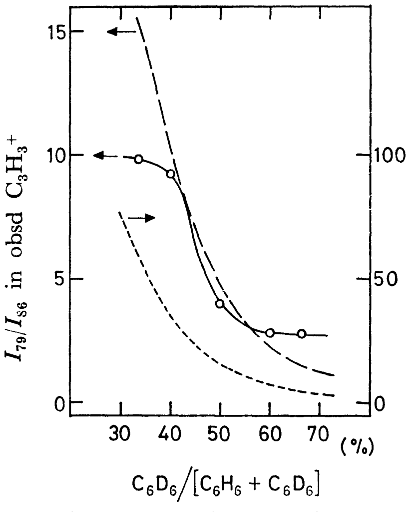
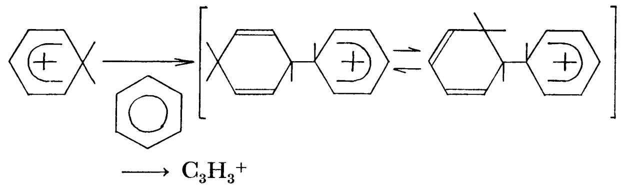


Fig. 9. Dependence of I_{79}/I_{86} on the ratio of the concentration of C_6D_6 to that of $C_6H_6 + C_6D_6$. Calculated (π-type complex), ----; calculated (σ-type complex), ———; observed, —O—.

On the other hand, the π-type complex is considered to dissociate into a protonated parent ion and a benzene molecule, and therefore, does not contribute to $C_3H_3^+$ formation.

In conclusion, the mechanism of $C_3H_3^+$ formation in gaseous benzene is explained by the following reaction path:



Experimental

The ICR spectra were obtained with a JEOL JIC-2M spectrometer, and the ICR cell was of a three-section square type similar to conventional ones.[9] Single-resonance spectra were obtained by fixing the frequency of the marginal oscillator and sweeping the magnetic field using field-modulation or energy-modulation phase-sensitive detection modes. Double-resonance experiments were performed by sweeping the frequency of the irradiating oscillator using a pulsed modulation mode for all reaction studies. The experimental conditions were as follows: energy of ionizing electrons 70 eV, trapping voltage 0.25 V, analyzer drift voltages −0.4 and 0.2 V, source drift voltages −2.5 and 0 V, observed of electric field and frequency 0.05 V/cm and 122.837 kHz and modulation frequency 80 Hz.

The analyzer chamber was baked at 150 °C for hours and evacuated below 2×10^{-7} Torr prior to performing the reported studies. Pressure was measured using an ionization vacuum gauge of the Bayard-Alpert type.

Benzene of special reagent grade (Wako Pure Chem. Ind., Ltd.) was purified by trap-to-trap distillation and the purity (>99.99%) was checked by gas-chromatography before use. Hexadeuterobenzene for spectroscopy (E. Merck, >99%D) was used without further purification. The samples were degassed under vacuum utilizing multiple freeze-pump-thaw cycles prior to introduction into the spectrometer.

Appendix

a) Formation of $C_6D_7^+$ in Benzene-d$_6$. For ICDR studies on benzene-d_6 and benzene, the following results were obtained. The irradiation of $C_6D_6^+$ at m/e 84 caused an increase in the intensity of $C_6D_7^+$. This ICDR result indicates that the $C_6D_7^+$ is formed by the ion-molecule reaction:

$$C_6D_6^+ + C_6D_6 \rightarrow C_6D_7^+ + N. \qquad (A1)$$

However, the ICDR peak of $C_6H_6^+$ corresponding to the reaction producing $C_6H_7^+$ was not confirmed due to the proximity of the observing $C_6H_7^+$ frequency to the irradiating $C_6H_6^+$ frequency. The reaction for $C_6H_7^+$ formation, however, could be considered to be the same as reaction (Al).

b) Calculation of the I_{79}/I_{86} Ratio of ICDR Spectral Intensities. $C_3H_3^+$ is formed by reactions (2) and (3). Then, the I_{79}/I_{86} ratio when $C_3H_3^+$ is observed is calculated to be

$$\frac{I_{79}}{I_{86}} = \frac{P(C_6H_7^+)\{C(C_6H_6)\times P[C_{12}H_{13}^+]+C(C_6D_6)\times P[C_{12}H_7D_6^+]\}}{P(C_6D_7^+)\times C(C_6H_6)\times P[C_{12}H_6D_7^+]}, \qquad (A2)$$

where

$$P(C_6H_7^+)=C(C_6H_6^+)\times C(C_6H_6)$$

with $P(C_6H_7^+)$ representing the probability that $C_6H_7^+$ is formed, $C(C_6H_6^+)$ the benzene ion concentration, $C(C_6H_6)$ the benzene concentration, $P[C_{12}H_{13}^+]$ the probability that $C_3H_3^+$ is formed from the complex $[C_{12}H_{13}^+]$ and the other symbols are defined in the same manner.

For example, in the case of a C_6H_6–C_6D_6 mixture in the ratio of 1 : 1, $C_6D_7^+$ is formed by reaction (Al). The concentration of C_6D_6 is 1/2, and that of $C_6D_7^+$ is also 1/2. Therefore, $P(C_6D_7^+)=1/4$. Similarly, $P(C_6H_7^+)=1/4$. Let us assume that $C_3H_3^+$ is formed by the random combination of three carbon and three hydrogen atoms in the π-type complex. The probability that $C_3H_3^+$ is formed from the complex $[C_{12}H_{13}^+]$ is

$$P[C_{12}H_{13}^+] = \frac{{}_{12}C_3\times{}_{13}C_3}{{}_{25}C_6} = \frac{286}{805}.$$

Similarly,

$$P[C_{12}H_7D_6^+] = \frac{{}_{12}C_3\times{}_{7}C_3}{{}_{25}C_6} = \frac{1}{23}$$

and

$$P[C_{12}H_6D_7^+] = \frac{{}_{12}C_3\times{}_{6}C_3}{{}_{25}C_6} = \frac{1}{161}.$$

By substituting the actual values into Eq. A2, we obtain

$$\frac{I_{79}}{I_{86}} = \frac{16.0}{1}.$$

In the case of a σ-type complex, let us assume that $C_3H_3^+$ is formed by a combination of the three adjoining carbon and the three adjoining hydrogen atoms in the σ-type complex. There are 16 combinations of the three adjoining carbon atoms. However, the number of combinations of the three adjoining hydrogen atoms differ for each complex. There are 19 combinations of the three adjoining hydrogen atoms in the complex $[C_{12}H_{13}^+]$, 9 such combinations in the complex $[C_{12}H_7D_6^+]$, and 6 such combinations in the complex $[C_{12}H_6D_7^+]$, respectively. Therefore, the probabilities that $C_3H_3^+$ is formed from each σ-type complex are equal to $P[C_{12}H_{13}^+]=19/16$, $P[C_{12}H_7D_6^+]=9/16$, and $P[C_{12}H_6D_7^+]=6/16$. By substituting the actual values into Eq. A2, we finally obtain $I_{79}/I_{86}=4.7/1$.

References

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2) F. H. Field, P. Hamlet, and W. F. Libby, *J. Am. Chem. Soc.*, **89**, 6035 (1967); *ibid.*, **91**, 2839 (1969).

3) S. Wexler and R. P. Clow, *J. Am. Chem. Soc.*, **90**, 3940 (1968).

4) A. Giardini-Guidoni and F. Zocchi, *Trans. Faraday Soc.*, **64**, 2342 (1968).

5) C. Lifshitz and B. G. Reuben, *J. Chem. Phys.*, **50**, 951 (1969).

6) J. Collin and F. P. Lossing, *J. Am. Chem. Soc.*, **79**, 5848 (1957).

7) J. L. Franklin and A. Mogenis, *J. Phys. Chem.*, **71**, 2820 (1967).

8) R. Breslow and J. T. Groves, *J. Am. Chem. Soc.*, **92**, 984 (1970).

9) (a) J. H. Futrell, "Dynamic Mass Spectrometry," Vol. 2, ed. by D. Price, Heyden & Son, New York (1971); (b) J. L. Beauchamp, *Ann. Rev. Phys. Chem.*, **22**, 527 (1971); (c) M. B. Comisarow and A. G. Marshall, *J. Chem. Phys.*, **62**, 293 (1975).