BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2261—2263 (1971)

Initiation Mechanism of Radiation-Induced Ionic Polymerization of Isobutene Studied by Ion Cyclotron Resonance

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(Received January 20, 1971)

Radiation induced polymerization of isobutene has been proved to proceed in cationic mechanism in liquid[1] and gas phases.[2] Investigation by high pressure mass spectrometer has been carried out to elucidate the initiation mechanism.[3] However, detailed processes of the ion-molecule reaction in isobutene, such as the role of fragment ions in the initiation, have not yet been made clear because of the difficulty to identity complex ion-molecule reactions by ordinary mass spectroscopy.

Recently, ion cyclotron resonance (ICR) technique has been successfully applied to analysis and interpretation of the complex ion-molecule reactions.[4] In this note we present the results obtained by the ICR study on isobutene and clarify the initiation mechanism of the radiation induced polymerization

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[1] J. J. Sparapany, *J. Amer. Chem. Soc.*, **88**, 1357 (1966).

[2] H. Okamoto, K. Fueki, and Z. Kuri, *J. Phys. Chem.*, **71**, 3222 (1967).

[3] V. Aquilanti, A. Galli, A. Giardini-Guidoni, and G. G. Volpy, *Trans. Faraday Soc.*, **63**, 926 (1967).

[4] For examples, a) J. L. Beauchamp, L. R. Ander, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **89**, 4569 (1967). b) J. M. S. Henies, *ibid.*, **90**, 844 (1968). c) G. A. Gray, *ibid.*, **90**, 6002 (1968). d) M. T. Bowers, D. E. Elleman, and J. L. Beauchamp, *J. Phys. Chem.*, **72**, 3599 (1968). e) S. E. Burttrill, Jr., *J. Chem. Phys.*, **50**, 4125 (1969). f) M. T. Bowers, D. D. Ellman, and J. King, Jr., *ibid.*, **50**, 4787 (1969).

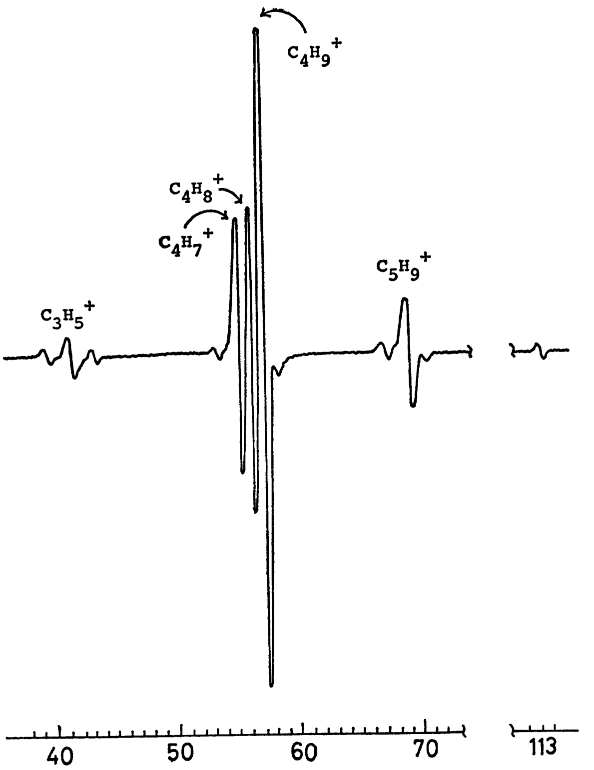

Fig. 1. Ion cycrotron single resonance spectrum of isobutene at 3×10^{-5} Torr.

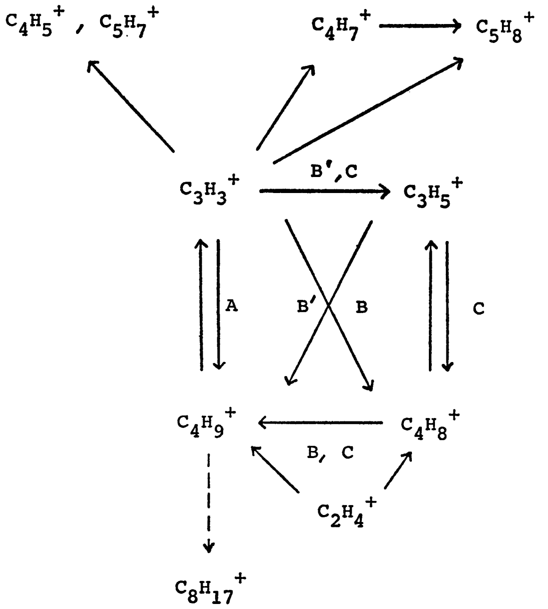

Fig. 2. Reaction scheme in isobutene observed by the ion cyclotron double resonance. Arrows show the ion-molecule reactions with isobutene. Solid arrows mean the reaction demonstrated by the ICR double resonance and broken arrow is a process deduced from the results.

in gas phase.

The ion cyclotron resonance spectrometer, which was constructed by the Japan Electron Optics Laboratory and utilized in this experiment, was a type similar to the conventional one.[4a)] Isobutene was purified by passing it through a column of potassium hydroxide followed by drying with sodium-potassium alloy.

An ion cyclotron single resonance mass spectrum observed at 3×10^{-5} Torr is shown in Fig. 1. Peaks in the spectrum correspond to those obtained at 6×10^{-3} Torr by a high pressure mass spectrometer.[3)] The relative intensity of the parent-plus-one ion ($m/e = 57$) is about fifty percent of that of total ions at 3×10^{-5}. It should be mentioned that the dimer ion ($m/e = 113$) is also observed at this pressure. Such ICR data indicate that ion-molecule reactions take place at very low pressures.

It was found that abundance of ions depends upon pressure, and the dependence observed from ICR differs from that of high pressure mass spectroscopy.[3)] The most remarkable contrast is that relative intensities of $C_4H_8^+$ and $C_4H_9^+$ show minimums at 6.5×10^{-5} and 9×10^{-5} Torr, respectively, though no minimum appears in mass spectroscopy. The intensity of $C_4H_9^+$ decreases with the increase of pressure from 3.0×10^{-5} to 9.0×10^{-5} Torr, but at higher pressures it increases with the increase of pressure. The pressure dependence of $C_3H_3^+$ also differs from that observed by the high pressure mass spectrometer. In contrast to $C_4H_9^+$, formation of $C_3H_3^+$ reaches a maximum at 9×10^{-5} Torr.

The ion-molecule reactions of these ions were studied by double resonance experiments. The over-all scheme is summarized in Fig. 2. $C_4H_9^+$ reacts with isobutene through two processes, the addition reaction to form dimer ion ($m/e = 113$)[5)] and the decomposition reaction to $C_3H_3^+$. The decomposition reaction is a sole process to produce secondary $C_3H_3^+$. Thus, the increase of the intensity of $C_3H_3^+$ with the increase of pressure implies that the decomposition of $C_4H_9^+$ by collision with isobutene into $C_3H_3^+$ is the dominant process at pressure below 9×10^{-5} Torr. Simultaneous appearance of the maximum of $C_3H_3^+$ with minimum of $C_4H_9^+$ at 9×10^{-5} Torr suggests additional paths besides the direct production of $C_4H_9^+$ from $C_3H_3^+$. The paths, including the direct production, are indicated as A, B, B′, and C in Fig. 2. Each step of these paths has been confirmed by double resonance experiments. The indirect paths involve one or two intermediates and the reactions through these paths are higher orders, *viz.*, the second order for paths of either B or B′, the third order for path C. Since the reactions of the higher orders become effective at higher pressures, contribution of the indirect paths to the production of $C_4H_9^+$ is more enhanced at higher pressures than at lower pressures. The maximum in pressure variation of the formation of $C_4H_9^+$ can be explained by assuming the competition among the reactions through the various paths described in Fig. 2.

$C_4H_9^+$ has been considered to be produced by a proton transfer from the parent ion.[1,2)] Study of high pressure mass spectroscopy[3)] suggested that a proton transfer from the other primary ions was also important to account for a large intensity of $C_4H_9^+$.

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5) We could not confirm the process producing $C_8H_{17}^+$ by the double resonance experiment, because the abundance of $C_8H_{17}^+$ was very small.

The double resonance experiments clearly show that $C_4H_9^+$ is produced from $C_2H_4^+$, $C_3H_3^+$, $C_3H_5^+$, and $C_4H_8^+$. These fragment ions must play important roles in the initiation process of the polymerization induced by γ-irradiation in gas phase, because the ion-molecule chain which starts from *t*-butyl ion ($m/e=57$) is possibly the first step of polymerization.