An Estimation of the Propagation Rate Constant for the Radiation-Induced Polymerization of Gaseous Isobutene

Yasuyuki Noro, Kenji Fueki and Zen-ichiro Kuri

Department of Synthetic Chemistry, Faculty of Engineering Nagoya University, Chikusa-ku, Nagoya

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In a previous paper,¹⁾ we have shown that the cationic mechanism dominates in the radiation-induced polymerization of gaseous isobutene. Since it is well established by a number of studies in the field of radiation chemistry that ammonia is an efficient proton acceptor and neither a radical nor electron scavenger, ammonia may be used for an estimation of the propagation rate constant on the basis of the assumption that the mechanism of radiation-induced polymerization of gaseous isobutene is cationic.

In this communication, we report the propagation rate constant and the mean lifetime of the propagating ion estimated in a quantitative study of the effect of ammonia on this polymerization.

Figure 1 shows a plot of the *G*-value for monomer consumption *vs.* the mole ratio of isobutene to ammonia at 500 Torr and 20°C. In Fig. 1, a straight line can be drawn through the experimental points at low concentrations of ammonia. We put on this result an interpretation that the linear portion of the curve indicates the retardation by ammonia of the polymerization due to ions surviving as a result of diffusional loss of electrons on the vessel wall and the curved portion at higher concentrations of ammonia corresponds to that due to ions which undergo gas-phase recombination.

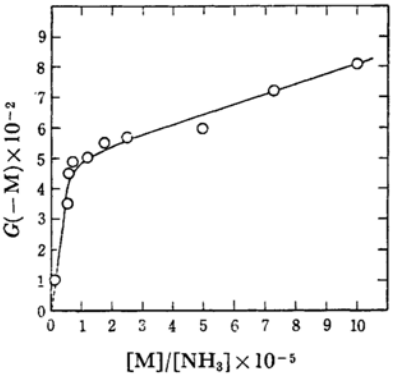

Fig. 1. The dependence of the polymerization yield on the mole ratio of isobutene to ammonia.

We apply the Klots-Anderson theory²⁾ to an estimation of the fraction of gas-phase recombination, *f*. A dimensionless parameter, κ, is defined by $\kappa^2=R^4I\alpha/D_+D_-$, where R is the radius of the vessel, I is the rate of ion-pair generation per unit volume, α is the bimolecular recombination coefficient, and D_+ and D_- are the diffusion coefficients for positive ions and electrons respectively. Taking $R=4$ cm, $I=2\times10^{11}$ ions cm^{-3}sec^{-1}, $\alpha=10^{-7}$ cm^{3}ions^{-1}sec^{-1}, $D_+=3\times10$ cm^{2}sec^{-1} and $D_-=2\times10^2$ cm^{2}sec^{-1}, we obtain $\kappa=920$. From Fig. 1 of Klots and Anderson, it can be estimated that this corresponds to 90% gas-phase recombination, $f=0.9$, and 10% loss by diffusion, $1-f=0.1$.

We can now evaluate the propagation rate constant, k_p, using the relation³⁾

$$G(-\mathrm{M}) = G_x\frac{k_p}{k_r}\frac{[\mathrm{M}]}{[\mathrm{NH_3}]} + G_c(-\mathrm{M})\,, \qquad (1)$$

where k_r is the rate constant for termination by ammonia, which is of the order $10^{10\pm1}$ M^{-1}sec^{-1}, and $G_x=G_i\times(1-f)$, G_i is the ion-pair yield per 100 eV absorbed. From the slope of the linear portion in Fig. 1 and Eq. (1), we obtain $k_p=8.3\times10^{6\pm1}$ M^{-1}sec^{-1}.

The mean lifetime of a propagating ion during growth in the pure monomer is given by

$$\tau_p = G_0(-\mathrm{M})/G_xk_p[\mathrm{M}]\,. \qquad (2)$$

Using the value $\mathrm{G_0}(-\mathrm{M})=1000$ for pure isobutene and the previous values for G_x and k_p, we obtain $\tau_p=10^{-2\pm1}$ sec.

Since there is some ambiguity in the recombination coefficient and the diffusion coefficients in addition to the rate constant for termination by ammonia, the values for k_p and τ_p should be taken as representing the order of their magnitudes.

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3) M. A. Bonin, W. R. Busler and F. Williams, *J. Am. Chem. Soc.*, **87**, 199 (1965).