Kinetics of Ionic Processes in the Radiolysis of Liquids. V.[1] Cationic Polymerization of Isobutylene under Anhydrous Conditions[2-4]

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Abstract: By resorting to a rigorous experimental technique, it has been shown that the rate of the radiation-induced polymerization of isobutylene under anhydrous conditions is proportional to the 0.55 power of dose rate. In these circumstances, the kinetic chain lengths are extremely large with $G(-m)$ values exceeding 10^8 molecules/100 eV at the lowest dose rate. These results are perfectly explicable on the basis of polymerization by free ions. The rate of polymerization is almost independent of temperature between 40 and $-78°$, and the rate constant for propagation at 0° is estimated to be $1.5 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. Chain transfer to monomer governs the molecular weight of the polymer which decreases as the polymerization temperature is raised. The results of this work cast considerable doubt on the interpretation of previous studies on the radiation-induced polymerization in the presence of solid additives.

Ions generated in liquid hydrocarbons by high-energy radiation are kinetically distinguishable as free ions and correlated pairs of ions. The former group achieves initial separation by diffusion and then recombines at random according to homogeneous second-order kinetics, while the latter undergoes a process which has become known as geminate recombination. Of these two groups, the free ions are generally produced with smaller yields,[5] but they are endowed with mean lifetimes which are longer by many orders of magnitude. Consequently, the space-time average concentration of ions present during irradiation is made up almost exclusively of free ions.[6]

The role of free ions can become extremely important in the radiation chemistry of hydrocarbons when ionic chain reactions take place. However, in order that the free ion should propagate over a period commensurate with its physical lifetime, τ_{ss}, as determined by charge neutralization, the concentration [X] of reactive impurities must be very low. Essentially, this condition takes the form that the product $k_{tX}[X]$, where k_{tX} is the rate constant, must be less than $1/\tau_{ss}$. Since τ_{ss} is typically 10^{-3} sec or longer at dose rates of practical interest,[6] this means that [X] must be reduced below $10^{-7}\ M$ if we adopt the diffusion-controlled value of $10^{10}\ M^{-1}\ \text{sec}^{-1}$ for k_{tX} in mobile liquids.

Studies of radiation-induced ionic polymerization have shown that the rates are frequently limited by the residual water content of the monomer.[7] The original purpose of the present work was to determine whether the rate of polymerization of isobutylene under homogeneous conditions could be increased above the values recorded in the literature by resorting to more exhaustive drying procedures. Our curiosity had been aroused by the frequent claims[8] that the presence of added solids (zinc oxide, alumina, or silica gel) during irradiation increased the rate of isobutylene polymerization by orders of magnitude, and that this effect was attributable in some way to the direct participation of the solid in the mechanism of polymerization. Finally, it was also felt that this work might contribute to our basic understanding of the reactions of positive ions in the condensed phase since it is well known that isobutylene polymerization is initiated only by cationic catalysts.[9]

Experimental Section

Materials. Isobutylene was obtained as Research Grade (99.59 mol %) from the Phillips Petroleum Co. Sodium–potassium liquid alloy corresponding to the eutectic composition (78 wt % potassium) was supplied by MSA Research Corp.

Preparation of Samples. It should be clear from the introductory remarks that the perfection of an unusually stringent drying technique was vital to the objective of this investigation. The apparatus was developed by modification of two earlier designs which for one reason or another proved to be unsatisfactory.[3] Only the final and successful version of this experimental technique will be described here.

The apparatus consisted of two complete vacuum systems connected end-to-end through a metal valve positioned immediately outside one of the oven portholes, as shown in Figures 1 and 2. One vacuum line (Figure 1) was used to treat the monomer in the degassing and drying operations, while the other system (Figure 2) was made up of an all-glass manifold with attached sample tubes, the entire unit being suspended inside an oven and connected to a high-capacity pumping installation (2-in. i.d. components from Consolidated Vacuum Corp.) capable of reaching a vacuum of 10^{-7} Torr. The preparative line (Figure 1) was constructed from flasks and tubing of Pyrex glass and from Nupro bellows valves fitted with Kovar seals. A round-bottomed flask containing 50 g of sodium–potassium alloy and fitted with an electric heating mantle was interposed between the cylindrical storage flasks and the connection leading to the bakeable vacuum system. Additional details of vacuum-line construction have been given elsewhere.[3]

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[1] Part IV: F. Williams, *J. Chem. Phys.*, **48**, 4077 (1968).

[2] This work was supported by the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-2968. This is AEC Document No. ORO-2968-43.

[3] Based on the M.S. thesis of R. B. Taylor, University of Tennessee, 1968.

[4] A preliminary communication has been published: R. B. Taylor and F. Williams, *J. Am. Chem. Soc.*, **89**, 6359 (1967).

[5] W. F. Schmidt and A. O. Allen, *J. Phys. Chem.*, **72**, 3730 (1968).

[6] For a discussion of the kinetics of ionic reactions in liquid hydrocarbons and for pertinent references, see F. Williams in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience Division, John Wiley & Sons, Inc., New York, N. Y., 1968, p 515.

[7] (a) T. H. Bates, J. V. F. Best, and F. Williams, *Nature*, **188**, 469 (1960); *Trans. Faraday Soc.*, **58**, 192 (1962); *J. Chem. Soc.*, 1531 (1962); (b) a review of recent work on the radiation-induced ionic polymerization of dry monomers is given in ref 6.

[8] (a) A review of the earlier work on the radiation-induced polymerization of isobutylene is given by S. H. Pinner, "The Chemistry of Cationic Polymerization," P. H. Plesch, Ed., Pergamon Press Ltd., Oxford, 1963, p 611; (b) F. L. Dalton, *Polymer*, **6**, 1 (1965); J. A. Bartlett and F. L. Dalton, *ibid.*, **7**, 107 (1966).

[9] J. P. Kennedy and R. M. Thomas, *J. Polymer Sci.*, **49**, 189 (1961); **55**, 311 (1961).

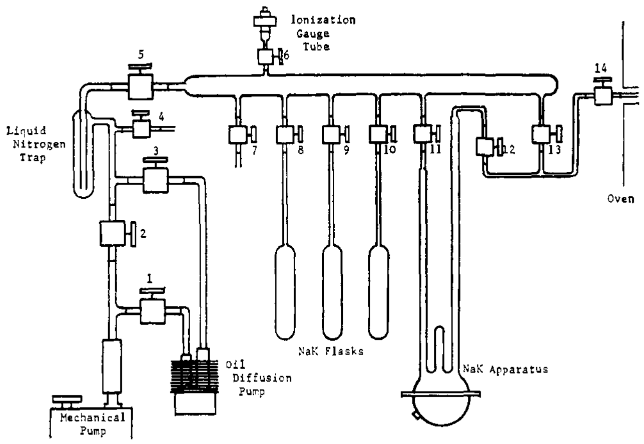

Figure 1. Vacuum system for pretreatment and drying of isobutylene monomer. Valves 1, 2, 3, and 5 were Nupro bellows valves SS-8BG-SW and valves 4 and 6 through 14 were Nupro bellows valves SS-4BG-SW.

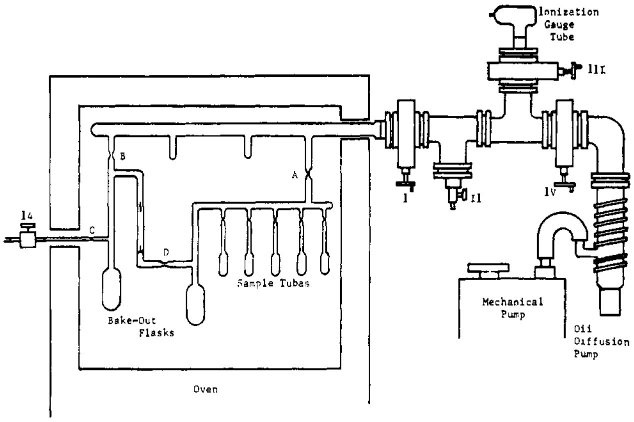

Figure 2. Vacuum system for bakeout of flasks and sample tubes used for irradiation. A, B, C, and D indicate glass constrictions at which points the seals were made (see text). Valves I, III, and IV were Consolidated Vacuum Corp. stainless steel gate valves Type VCS-21A and had a screw action. Valve II was a small Nupro valve with a Teflon stem tip. Valve 14 is the same as that shown in Figure 1 and connects the two vacuum systems together.

After assembly inside the oven (Model B100680, Gruenberg Electric Co., Inc.), the irradiation tubes and the remainder of the glass system shown in Figure 2 were evacuated at 500° for a typical bake-out period of 150 hr until the ionization gauge indicated a pressure of $(1.0–2.5) \times 10^{-7}$ Torr. During this time, the connecting valve to the preparative line was closed. When the oven had cooled after completion of the bake-out process, the glass system was sealed off at two points from the main manifold. By this stage, isobutylene had been introduced into the other line and thoroughly degassed by repeated freeze–pump–thaw cycles after each transfer *in vacuo* between the cylindrical storage flasks containing sodium–potassium alloy. Between each transfer, the walls of the receiving flask were coated with a fresh surface mirror of the alkali metals. Then, with the liquid isobutylene held at $-40°$ or above in one of the reservoir flasks, the vapor was admitted continuously over refluxing sodium–potassium alloy at 300° in the three-necked flask (Figure 1) and condensed at $-196°$ into the first reservoir in the baked-out glass apparatus (Figure 2). This transfer was generally rather slow and occurred at the rate of about 10 ml/hr. After repeated degassing of the condensate by pumping through the flask containing the hot alloy, the remaining connection was sealed off and the glass unit removed from the oven. The concluding steps were of a routine character and involved breaking the seal between the two reservoirs, distilling the entire sample into the second reservoir, and finally filling the individual sample tubes in rotation by vacuum distillation. Before sealing off at the glass constrictions, the isobutylene was always cooled to $-196°$.

γ Irradiations. A Gammacell-200 source was modified to allow irradiations to be carried out at one of three reproducible dose rates, each one corresponding to a fixed position of the sample chamber relative to the cobalt source. As of April 1, 1968 and for the particular experimental configuration used in this work, the dose rates were determined by Fricke dosimetry in 0.8 N H_2SO_4 and then calculated for isobutylene to be 4.97×10^{15}, 6.90×10^{14}, and 6.51×10^{13} eV g^{-1} sec^{-1}, the former of these corresponding to the standard irradiation position. By the use of additional lead shielding around the sample in the chamber position farthest removed from the source, the dose rate, as measured in Oct 1967, was reduced to 5.77×10^{12} eV g^{-1} sec^{-1}. An even lower dose rate of 5.3×10^{11} eV g^{-1} sec^{-1} was made available to us in a cobalt-60 source at the Oak Ridge National Laboratory through the courtesy of Dr. C. J. Hochanadel. In this case the average dose rate for isobutylene was calculated from an ionization measurement of 0.52 R min^{-1} in air carried out with a Victoreen condenser r-meter (Model 70), employing the conversion factor of 0.87 rad/R for air as well as the usual proportionality between γ dose and electrons per gram of absorber. The dose dates were adjusted to allow for the radioactive decay of the cobalt-60 according to the half-life of 5.3 years.

All irradiations were carried out with the isobutylene sample at a constant temperature inside a dewar flask. Since the irradiation times were generally only a few minutes in duration, no particular problem of temperature drift was encountered by using liquid baths which had been precooled to the desired temperature.

Polymer Analysis and Characterization. The amount of polymer produced in each run was determined gravimetrically. After evaporation of most of the monomer at room temperature, the polymer sample was heated to 90° in a vacuum oven until a constant weight was attained. Molecular weight determinations by light scattering and membrane osmometry were carried out by Arro Laboratories, Inc., Joliet, Ill.

Results

Although the desirability of reproducible results in studies of radiation-induced ionic polymerization is unquestionable, there has been a general tendency to put undue stress on this one facet to the exclusion of other considerations. To illustrate the point we wish to make, reference is made to the early studies[8] on isobutylene which indicated a fair degree of reproducibility with $G(-m)$ values at $-78°$ of the order of 10^3. It is now clear that such results are characteristic of wet isobutylene, and that when more exhaustive drying techniques are applied, the rates become higher. However, the attainment of good reproducibility becomes progressively more difficult as the rates of polymerization increase unless the entire preparative technique is very thorough.[6] In some preliminary work[3] on isobutylene using a much less rigorous experimental method than the one described in this report, we obtained $G(-m)$ values at $-78°$ up to 6×10^4. These results[10] served mainly to convince us of the need to develop an improved technique.

In Table I we present a compilation of data which includes a survey of results obtained under identical irradiation conditions. This illustrates the degree of reproducibility attained in this work, all samples having been prepared by the standard method outlined in the Experimental Section. The calculation of rates of polymerization in Table I is based on the assumption that a linear relation exists between conversion and

(10) (a) *Cf.* K. Ueno, K. Hayashi, and S. Okamura, *Polymer Letters*, **5**, 569 (1967); K. Ueno, A. Shinkawa, K. Hayashi, and S. Okamura, *Bull. Chem. Soc. Japan*, 40, 421 (1967). These authors have reported $G(-m)$ values for carefully dried isobutylene in the region of 10^5 with an average value of 1.5×10^5 from four runs at $-78°$. (b) The difficult problem of reducing the concentration of reactive impurities in order to observe the true (unquenched) kinetic characteristics of transient species in liquids has also been encountered in studies of the hydrated electron (E. J. Hart, S. Gordon, and E. M. Fielden, *J. Phys. Chem.*, 70, 150 (1966)) and of triplet states of aromatic molecules (S. C. Tsai and G. W. Robinson, *J. Chem. Phys.*, **49**, 3184 (1968)).

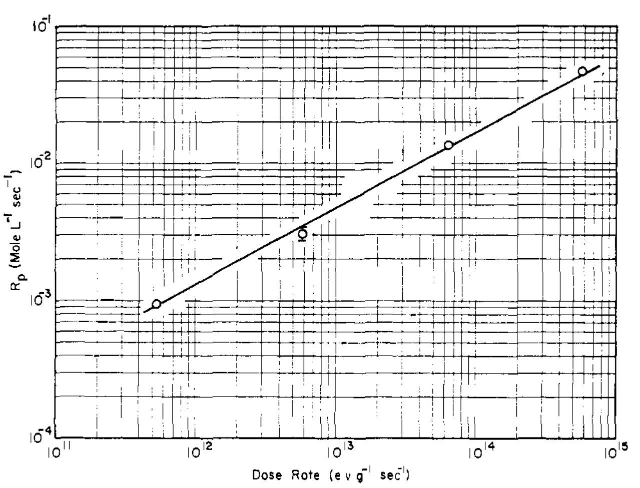

Figure 3. Dose rate dependence of rate of isobutylene polymerization at 0°. The horizontal bars attached to one circle represent the spread of valves about the mean. In the other cases, the spread was within the diameter of the open circles. A total of 11 runs was carried out with samples from three batches of isobutylene.

time. In order to verify this point by working with separate samples, the rates must be highly reproducible, and it is for this reason that each set of results in Table II refers to samples taken from the same batch of monomer. Within the limitations set by the degree of reproducibility, it appears that the conversion is approximately proportional to the irradiation time at constant dose rate and temperature, provided that the conversions are not unduly excessive.

Table I. Rates and $G(-m)$ Yields for the Polymerization of Isobutylene at 0°

Code batch-sample no.	Irradiation time, sec	Dose rate, eV g^{-1} sec^{-1}	Conversion, wt %	Rate, M sec^{-1}	$G(-m)$, molecules/100 eV
10-2	900	5.3×10^{11}	7.5	9.2×10^{-4}	1.68×10^{8}
10-4	900	5.3×10^{11}	7.8	9.5×10^{-4}	1.75×10^{8}
12-2	900	5.8×10^{12}	27.6	3.38×10^{-3}	5.7×10^{7}
12-4	900	5.8×10^{12}	21.9	2.68×10^{-3}	4.5×10^{7}
4-4	300	6.2×10^{13}	41.7	1.53×10^{-2}	2.39×10^{7}
6-2	300	6.2×10^{13}	29.9	1.10×10^{-2}	1.72×10^{7}
6-4	300	6.2×10^{13}	31.1	1.14×10^{-2}	1.80×10^{7}
8-4	300	6.2×10^{13}	27.3	1.00×10^{-2}	1.58×10^{7}
10-1	300	6.2×10^{13}	36.8	1.35×10^{-2}	2.14×10^{7}
10-5	300	6.2×10^{13}	39.4	1.45×10^{-2}	2.28×10^{7}
11-1	300	6.1×10^{13}	34.0	1.25×10^{-2}	1.98×10^{7}
12-1	300	6.1×10^{13}	37.4	1.37×10^{-2}	2.19×10^{7}
10-3	60	6.8×10^{14}	26.9	5.0×10^{-2}	7.1×10^{6}
11-3	60	6.7×10^{14}	24.1	4.4×10^{-2}	6.4×10^{6}
12-3	60	6.7×10^{14}	25.1	4.6×10^{-2}	6.7×10^{6}

Table II. Conversion to Polymer *vs.* Irradiation Time at 0 and −78°

Code batch-sample no.	Temp, °C	Time, sec	Dose rate, eV g^{-1} sec^{-1}	Conversion, wt %
4-3	0	600	6.2×10^{13}	66.5
4-4	0	300	6.2×10^{13}	41.7
9-3	0	58	6.8×10^{14}	13.3
9-1	0	27.5	6.8×10^{14}	6.6
3-3	−78	600	6.3×10^{13}	13.4
3-4	−78	300	6.3×10^{13}	7.3

The dose rate dependence of the rate of polymerization at 0° is illustrated in Figure 3 by the combined results from three batches of monomer, and the slope of the logarithmic plot is 0.55. It is significant that these high rates are very nearly proportional to the 0.50 power of dose rate, as predicted by the free ion mechanism[11] when impurity termination becomes negligible. At −78°, the R_p values were somewhat less reproducible (*vide infra*), but if we select the average of the four highest rates at each dose rate, we obtain 5.5×10^{-3} M sec^{-1} and 1.83×10^{-2} M sec^{-1} at 6.2×10^{13} and 6.4×10^{14} eV g^{-1} sec^{-1}, respectively. Each of these R_p values is lower than the corresponding average value at 0° by a factor of about 2.5, but the power of the dose rate dependence is hardly altered. It might be added that it is justifiable to consider the highest rates as the most meaningful in discussing the limiting form of the dose rate dependence.[6,11]

A summary of the results for the temperature dependence of the polymerization rate is given in Table III. It is clear that neither the average nor the highest rates fit an Arrhenius relation over the entire range. The highest rates are within about a factor of 2 between −78 and 27° so it seems that any real activation energy is bound to be negligible. We encountered poorer reproducibility at −78° than at 0°, and this is reflected by the gap between the highest and average values in Table III. The results obtained at −138° just above the melting point (−140°) are an order of magnitude lower than those at the higher temperatures, but it is likely that this difference is attributable to a number of causes, including the possibility that the polymerization at −138° occurs for the most part in a semisolid matrix due to the rigidity of the polymer gel even at very low conversion.

Only a limited number of molecular weight measurements were made, but these (Table IV) show an unmistakable trend in the direction of higher molecular weights as the polymerization temperature is decreased. The same tendency was observed in the catalytic polymerization of isobutylene in solution[9] and also for the radiation-induced polymerization of bulk isobutylene in the presence of zinc oxide.[8]

Discussion

Much of the previous work on the radiation-induced polymerization of isobutylene both in the absence and presence of dispersed solids has been reviewed elsewhere,[6] so here we can focus on the main problem by summarizing the results of two studies that have led to conflicting interpretations. Kristal'nyi and Medvedev[12] showed that after pretreatment with zinc oxide or alumina, isobutylene underwent polymerization at about the same rate as in the presence of the solid, the highest $G(-m)$ value being 4×10^5 molecules/100 eV at −78° and a dose rate of 6×10^{14} eV g^{-1} sec^{-1}. Moreover, these authors[12] found that while addition of water to anhydrous isobutylene in concentrations as low as 1.6×10^{-3} mol % depressed the G value to *ca.* 1×10^3, subsequent treatment with zinc oxide restored the

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[11] F. Williams, Ka. Hayashi, K. Ueno, K. Hayashi, and S. Okamura, *Trans. Faraday Soc.*, 63, 1501 (1967).

[12] E. V. Kristal'nyi and S. S. Medvedev, *Vysokomol. Soedin.*, 7, 1373, 1377 (1965).

Table III. Effect of Temperature on the Radiation-Induced Polymerization of Isobutylene[a]

Number of runs	Temp, °C	R_p, M sec^{-1} Average	Highest	$G(-m)$, molecules/100 eV Average	Highest
3	27	8.5×10^{-3}	8.9×10^{-3}	1.41×10^{7}	1.47×10^{7}
13	0	1.06×10^{-2}	1.53×10^{-2}	1.65×10^{7}	2.39×10^{7}
3	−40	4.4×10^{-3}	8.4×10^{-3}	6.4×10^{6}	1.24×10^{7}
9[b]	−78	2.70×10^{-3}	1.07×10^{-2}	3.7×10^{6}	1.46×10^{7}
3	−138	4.4×10^{-4}	4.7×10^{-4}	5.5×10^{5}	5.9×10^{5}

[a] Irradiation time was 300 sec at a dose rate of 6.2×10^{13} eV g^{-1} sec^{-1}. [b] The average of the four highest rates at −78° gives $R_p = 5.5 \times 10^{-3}$ M sec^{-1} and $G(-m) = 7.5 \times 10^{6}$.

Table IV. Molecular Weights of Polyisobutylene[a]

Polymerization temp, °C	Conversion to polymer, wt %	Method of determination	Mol wt
40	25	Membrane osmometry	$\overline{M}_n = 25{,}500$
0	25	Membrane osmometry	$\overline{M}_n = 51{,}500$
−40	15	Membrane osmometry	$\overline{M}_n = 1{,}021{,}000$[b]
−78	20	Light scattering	$\overline{M}_w = 3{,}494{,}000$[c]

[a] Polymers were prepared by irradiation of isobutylene for 300 sec at a dose rate of 6.0×10^{13} eV g^{-1} sec^{-1}. [b] The osmotic pressure was very low and this value may not be very accurate. The data could be extrapolated somewhat differently to give a value as low as $\overline{M}_n \approx 300{,}000$. [c] After correction for dissymmetry.

G value to more than 1×10^5. Despite the apparent clarity of these observations,[13] one criticism which might be made is that the polymerization rates are at least a factor of 10 lower than the extrapolated value from Dalton's measurements[8b] at lower dose rates in the presence of zinc oxide. Thus it could still be argued that the rate is enhanced by the presence of the solid under certain conditions and that the role of zinc oxide is intrinsic to the mechanism of polymerization.[8b]

By obviating the need for contact with dispersed solids in the drying procedure and thereby eliminating the possibility that solid particles might be carried over to the irradiation cell by entrainment in the vapor, the present work is entirely free from any suspicion that the results are affected by finely divided solids. Yet, the polymerization rates listed in Table V compare favorably with the largest rates obtained by Dalton[8b] in the presence of zinc oxide. Thus it has been clearly demonstrated that the radiation-induced polymerization of isobutylene under anhydrous conditions proceeds with the very high rates that had been thought to be characteristic of the reaction in the presence of solid additives. As a corollary to this finding, it must be considered very probable that the solids serve only to remove traces of water from the system.

Table V. Rates of Radiation-Induced Polymerization of Isobutylene in the Absence and Presence of Zinc Oxide

Dose rate, eV g^{-1} sec^{-1}	Temp, °C	R_p, M sec^{-1} This work[a] (ZnO absent)	Ref 8b[b] (ZnO present)
1.0×10^{14}	−78	7.0×10^{-3}	8.8×10^{-3}
1.0×10^{14}	0	1.6×10^{-2}	
6.9×10^{12}	0	3.8×10^{-3}	1.38×10^{-3}[c]

[a] Interpolated from average rates at higher and lower dose rates. [b] Maximum rate as a function of zinc oxide composition. [c] Independent of temperature between 0 and −78°.

After having established that the reaction is homogeneous under our experimental conditions, we now turn to the more theoretical aspects of this work. A result of particular interest is the dependence of R_p on the 0.55 power of dose rate (Figure 3). According to the theory of radiation-induced polymerization by free ions,[11] this finding implies that the rates are near to the limiting values which would apply in the case of negligible impurity termination where R_p is given by relation 1.

$$R_p = \left\{\frac{R_i}{k_t}\right\}^{1/2} k_p[\mathrm{M}] \tag{1}$$

A calculation of the propagation rate constant, k_p, from the available data on the dose rate dependence of R_p requires that we know R_i, the rate of initiation, and k_t, the rate constant for termination by charge neutralization. The appropriate value of R_i may be evaluated by assuming that $G_i = 0.1$ since this yield of free ions is fairly typical for many hydrocarbons,[5] and it is extremely unlikely to be different by more than a factor of 10. An estimate of k_t is much more difficult to make because if the neutralization is diffusion controlled, the major contribution to this rate constant will come from the motion of the negative species whose nature is unestablished in this system. At least in the initial portion of its life, this negative species is likely to be a solvent-trapped electron rather than a molecular anion because there is no evidence in the literature that isobutylene behaves as an electron scavenger. Moreover, work in this and other laboratories has shown that trapped electrons are present in γ-irradiated hydrocarbon glasses containing isobutylene. Our knowledge of the structure and transport properties of solvent-trapped electrons is very limited, and only for the hydrated electron is there a fairly reliable value available for the diffusion constant,[14] $D(e_{aq}^-) = 4.5 \times 10^{-5}$ cm^2 sec^{-1} at 25°. Although some other significant differences must exist between the hydrated electron and the solvated electron in hydrocarbons, it seems reasonable to assume that the binding energy of the electron to the solvent is greater in water than in hydrocarbons, and consequently it might be expected that the diffusion constant would be greater in a hydrocarbon if the comparison were made at the same viscosity and temperature. On the other hand, it could also be argued that if the structure of the hydrated electron is more compact than for the electron in hydro-

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(13) These results[12] should be compared with the average $G(-m)$ value of 2.5×10^6 obtained in the present work from four runs carried out under conditions (−78° and 6.4×10^{14} eV g^{-1} sec^{-1}) corresponding almost exactly to those of ref 12.

(14) M. S. Matheson, Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, p 45.

carbons, application of Stokes' law would predict the opposite tendency. In view of these difficulties, we can only speculate about the value of the diffusion constant for the electron in isobutylene. A further problem is raised by the possibility that the solvated electron is converted to $O_2^{\dot{-}}$ or some other negative ion during the major part of the lifetime of the free ion. In the ensuing calculation, we use a value of 4×10^{-5} cm^2 sec^{-1} for D_-, the diffusion coefficient of the negative species, since this is fairly typical for small molecules in liquids of viscosities below 1 cP.

According to the simple theory of charge neutralization in nonpolar liquids,[6] the rate constant k_t is given by $4\pi r_c(D_+ + D_-)$. For singly charged ions, r_c is defined by $e^2/\epsilon kT$ and is equal to 3.06×10^{-6} cm for a dielectric constant $\epsilon = 2.0$ and $T = 273$°K. Hence for ions in isobutylene where $D_- >> D_+$, we obtain $k_t = 9.3 \times 10^{11}$ M^{-1} sec^{-1} at 0°. By means of eq 1, k_p may now be evaluated from the dose rate dependence of R_p shown in Figure 3. At a dose rate of 3.0×10^{14} eV g^{-1} sec^{-1}, the values of R_p and R_i are 3.0×10^{-2} and 3.1×10^{-10} M sec^{-1}, respectively, of which R_i is calculated from $G_i = 0.1$ molecule/100 eV and the density of isobutylene at 0°, 0.619 g ml^{-1}. The monomer concentration, [M], is 11.0 M, and k_p is then found to be 1.5×10^8 M^{-1} sec^{-1}. Because the temperature dependence of R_p (Table III) is too small to be statistically reliable, and since R_i, k_t, and [M] are all affected by temperature to different extents, it is impossible to obtain the temperature coefficient of k_p with any accuracy. All that can be said with confidence is that the activation energy for propagation is most unlikely to exceed 2 or 3 kcal/mol.

The previous calculation of the absolute value of k_p is subject to the various uncertainties in our estimates of k_t and R_i. However, these quantities enter the k_p expression as $(k_t/R_i)^{1/2}$, which means that the corresponding uncertainty in k_p is much reduced. It is difficult to conceive that our estimate of the ratio (k_t/R_i) is too high by a factor of 100, so there is very little doubt that k_p must be greater than 10^7 M^{-1} sec^{-1}. Essentially the same conclusion is reached if we compare the R_p value for isobutylene with the previously reported rates for the bulk polymerization of styrene and α-methylstyrene at a dose rate of 1.1×10^{14} eV g^{-1} sec^{-1}. For styrene (15°) and α-methylstyrene (0°), the highest R_p values[11,15] at this dose rate are 6.4×10^{-4} and 1.2×10^{-3} M sec^{-1}, respectively, as compared with 1.7×10^{-2} M sec^{-1} for isobutylene (Figure 3) at 0°. The comparison between isobutylene and α-methylstyrene is particularly appropriate because the exponent for the dose rate dependence of R_p at 0° is approximately 0.5 (± 0.05) in each case, and so there is good reason to believe that the limiting rates have been very nearly achieved. Then, from eq 1, it follows that the ratio of k_p values for the two monomers is given by the respective quotient of their polymerization rates if the other terms are sensibly the same. We take [M] to be the same at this level of approximation, and we assume the R_i values are similar. The value of k_t for isobutylene might be expected to exceed k_t for α-methylstyrene since the latter monomer is known to undergo electron capture to form a radical anion,[16] so we conclude that the ratio of the k_p values must be greater than ten in favor of isobutylene. From a previous kinetic treatment, k_p for α-methylstyrene was deduced to be 4×10^6 M^{-1} sec^{-1}, so the above analysis is consistent with the present value of 1.5×10^8 M^{-1} sec^{-1} for isobutylene. It can be concluded that isobutylene is an extremely reactive monomer in cationic homopolymerization.

The data on molecular weights of polyisobutylene as a function of the polymerization temperature (Table IV) reflect the importance of the proton-transfer reaction between propagating ion and monomer as the determining process in regard to the average degree of polymerization which is attained. This conclusion is supported by two observations. First, the degree of polymerization is always much smaller than the kinetic chain length represented by $G(-m)/G_i$, and, secondly, the average molecular weight is greatly reduced as the polymerization temperature is increased although the rate of polymerization is virtually unaltered. Thus it also follows that the activation energy for proton transfer to monomer is significantly greater than the activation energy for propagation. We hope to carry out a detailed study of the molecular weight distribution as a function of temperature, so further consideration of the monomer transfer reaction is deferred.

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