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Ion and Ion-Pair Contributions to the Polymerization of Tetrahydrofuran*

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ABSTRACT

The cationic polymerization of tetrahydrofuran is generally considered to be effected by an oxonium chain end in the form of an ion pair. Consideration of expected ionic dissociation constants of salts in typical solvents for these reactions suggests that appreciable concentration of free oxonium ions would be present under polymerization conditions. The dissociation constants of such salts have been measured in methylene chloride solution and shown to be near 4×10^{-6} , sufficiently high that a contribution to the polymerization by free ions could be expected. Rate constants for the propagation reaction of the polymerization initiated by triethyloxonium tetrafluoroborate have been measured, in both the presence and absence of the common-ion salt tetrabutylammonium tetrafluoroborate. From the dependence of the rate constant on the initiator concentration and from its reduction

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by varying concentration of the free common ions, it is possible to calculate the ion-pair rate constant to be $1.4 \times 10^{-3} \text{ M sec}^{-1}$ and the free oxonium ion rate constant to be $1.0 \times 10^{-2} \text{ M sec}^{-1}$.

It has been well established in living anionic polymerizations of hydrocarbon monomers in solvents of only moderate dielectric constant that the chain-propagation step is carried by both the free anion and the ion pair of the growing polymer chain-alkali metal salt [1]. In comparable cationic polymerizations, such as those of cyclic ethers by oxonium salts, where the lifetime of the growing chain is long compared with the time of polymerization, the propagation reaction is consistently said to proceed via an ion-pair reaction, even in solvents such as the chlorinated hydrocarbons with ϵ in the region of 10.

Consideration of the expected dissociation constants [2] of the polymerizing oxonium salts in these solvents would suggest that several percent free ions could well be present. Unless these free ions have a rate constant the same or lower than that of the ion pair, their presence should be detectable by kinetic measurements.

The polymerization of tetrahydrofuran initiated by oxonium tetrafluoroborate salts is a reaction which has been well studied [3, 4] and characterized as a typical living cationic polymerization with few complications in dry systems at not too high temperatures, apart from the rather high equilibrium monomer concentration due to its low heat of polymerization. Each initiator molecule has been shown to give one polymer chain after a rapid initiation reaction. To determine if a free-ion contribution is likely in this polymerization, conductance studies have been made on the system triethyloxonium tetrafluoroborate, methylene chloride, tetrahydrofuran at -0.5° . Measurements were also made of the rate of polymerization in the presence and absence of the common-ion salt tetrabutylammonium tetrafluoroborate, methods used with success in anionic systems [1, 5].

RESULTS AND DISCUSSION

The conductance of triethyloxonium tetrafluoroborate in methylene chloride was measured at three temperatures. The solutions were found to be stable for reasonable periods of time at 0° and below, as the conductances did not change significantly in 2 hr. The limiting equivalent conductances and dissociation constants derived are in Table 1, together with data for tetrabutylammonium tetrafluoroborate. Also in this table are the results of the conductance study on the low molecular weight polytetrahydrofuranoxonium tetrafluoroborate in

TABLE 1. Salt Conductivities

| Salt | Solvent | Temp (°C) | Λ_0^a | $10^6 K_D^a$ |
|---|--|-----------|---------------|--------------|
| $\text{Et}_3\text{O}^+\text{BF}_4^-$ | CH_2Cl_2 | - 0.5 | 121 | 5.4 |
| $\text{Et}_3\text{O}^+\text{BF}_4^-$ | CH_2Cl_2 | -10.9 | 114 | 5.3 |
| $\text{Et}_3\text{O}^+\text{BF}_4^-$ | CH_2Cl_2 | -22.1 | 99 | 6.0 |
| $\sim\text{OC}_4\text{H}_9^+\text{BF}_4^-$ ^b | CH_2Cl_2 | - 0.5 | 95 | 4.4 |
| $\text{Bu}_4\text{N}^+\text{BF}_4^-$ | CH_2Cl_2 | - 0.5 | 100 | 42 |
| $\text{Bu}_4\text{N}^+\text{BF}_4^-$ | CH_2Cl_2 , 65% - THF, 35% | - 0.5 | 91 | 39 |

^a Λ_0 and K_D were obtained by the method of successive approximations from the equation $1/\Delta F = (1/\Lambda_0) + (f^2 FAC/KA_0^2)$. The method and the terms are described by T. Shedlovsky, Tech. Org. Chem., **1**, 1651 (1949).

^bPoly(THF) salt; OC_4H_9 , tetrahydrofuranyl.

TABLE 2. Dielectric Constants of THF- CH_2Cl_2 Mixtures^a

| Vol % THF | ϵ | Vol % THF | ϵ |
|-----------|------------|-----------|------------|
| 0 | 9.9045 | 60.0 | 9.879 |
| 15.0 | 10.114 | 70.0 | 9.594 |
| 30.0 | 10.188 | 77.5 | 9.344 |
| 34.7 | 10.201 | 85.0 | 9.024 |
| 40.0 | 10.163 | 92.5 | 8.733 |
| 50.0 | 10.045 | 100 | 8.243 |

^aTemperature -0.5°.

methylene chloride, but as the preparation of this salt was questionable, these results should be treated with more reserve than others.

From these data it is evident that appreciable concentrations of free ions are present in these solutions at typical polymerization concentrations. For 10^{-3} M solutions, the degree of ionization would be near 7% for the oxonium salts and 20% for the tetrabutylammonium salt. If the free ion has a rate constant appreciably greater than that

of the ion pair, some effect should be seen on the kinetic order of the reaction.

The concentration of tetrahydrofuran in the reaction mixture for the kinetic studies was sufficiently high, 4.4 M, that it could be expected to change the dielectric constant of the reaction medium. This in turn might have significant effects on the dissociation constants of the reactants. The dielectric constants of a series of methylene chloride-tetrahydrofuran mixtures were measured at the reaction temperature, Table 2. Significant deviation from normal behavior was observed, the dielectric constant going through a maximum at a 2:1 mole ratio of methylene chloride to tetrahydrofuran. This could be interpreted in terms of some complex formation, but if so it is not reflected in density measurements of these mixtures, which exhibit almost ideal behavior. The reaction mixture is near the maximum of the dielectric constant curve, and this might be reflected in ionic dissociation constants higher than in the pure methylene chloride. The measured dissociation constant of the tetrabutylammonium salt in this mixture is in fact slightly lower than that found in the pure solvent. Unfortunately, it was not possible to measure the dissociation constants of oxonium salts in the mixture, but they also could be expected not to be lowered the severalfold expected if the solvents had exhibited ideal dielectric behavior.

The rate constants for the propagation are obtainable from the equation

$$-d[\text{THF}]/dt = k_p[\text{L.E.}]([\text{THF}]_0 - [\text{THF}]_e)$$

where k_p is the overall rate constant of propagation; $[\text{L.E.}]$ is the growing chain concentration, taken as the initial concentration of triethyloxonium tetrafluoroborate, a close approximation as shown by previous work; and $[\text{THF}]_e$ is the equilibrium tetrahydrofuran concentration, taken as 2.62 M, after Vofsi and Tobolsky.

The equations derived by Szwarc et al. [1], which govern the rate constants of propagation of mixed free-ion, ion-pair polymerizations are

$$k_p = k_{\pm} + (k_+ - k_{\pm})K_d^{1/2}/[\text{L.E.}]^{1/2}$$

where k_{\pm} is the ion-pair rate constant, k_+ is the oxonium ion rate constant, K_d is the ionic dissociation constant of the polymerizing oxonium salt, and in the presence of the common-ion salt

$$k_p = k_{\pm} + (k_+ - k_{\pm})K_d/[\text{BF}_4^-]$$

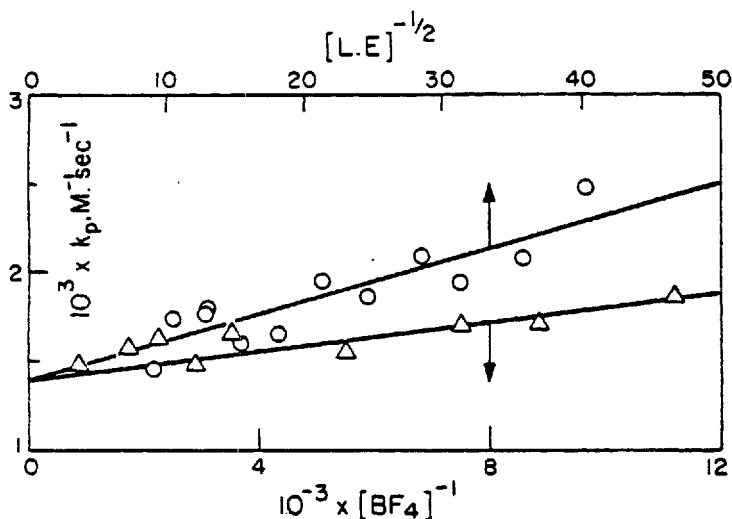


FIG. 1. Propagation rate constants in the oxonium ion polymerization of THF: (Δ) in the presence of added BF_4^- ion (\circ) in the absence of added salt.

where $[\text{BF}_4^-]$ is calculated from the dissociation constant of the tetrabutylammonium tetrafluoroborate.

The rate constants of the propagation reaction are shown in Fig. 1, plotted against the inverse half-power of the living end concentration, a plot designed to show the deviation from first-order kinetic dependence of the ion-pair reaction produced by the concurrent free-ion reaction. Also shown in Fig. 1 are similar rates in the presence of the common-ion salt, plotted against the inverse of the common-ion concentration, showing how it depresses the free-ion reaction.

It is evident from these results that although the bulk of the reaction is carried by the ion pair, a significant portion of the reaction is carried by the free ion. From these plots it is possible to derive from the intercept that the ion-pair rate is $1.40 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$. From the different dependence on k_p of the two slopes, the dissociation constant of the living end ion pair is 3.7×10^{-6} , and the free-ion rate constant is calculated as $1.0 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$.

This dissociation constant compares with the 5.4×10^{-6} found for triethyloxonium tetrafluoroborate and 4.4×10^{-6} for the low molecular weight polymer oxonium salt, both found from conductance data in pure methylene chloride. Although the kinetic figure is probably not too

reliable, it is evidently close to the expected value and lends credence to the suggestion that the free ions are participating in the reaction.

The calculated free-ion rate is only a factor of 7 greater than that of the ion pair, compared with the factor of 10^3 in the anionic polymerization of hydrocarbon monomers. This factor was found recently to be low also for the polymerization of episulfides [6] and was ascribed to the attack being on the carbon α to the charged atom instead of on the charged atom as in the anionic case. Here also the attack is at the carbon α to the charge. This ratio was also found to be low for the polymerization of ethylene oxide by potassium alkoxides in hexamethylphosphoramide [7], but in general the kinetic behavior was complex in this system.

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