is illustrated by the two examples quoted in the literature,[4] and another system of this kind was investigated in the course of our studies.

Interaction of tetranitromethane with α-methylstyrene in deuterated methanol was followed by nmr. The spectrum of the original olefin eventually disappears and the new one shows a singlet at δ 4.65 ppm (attributed to the CCH_2NO_2 protons), a singlet at δ 1.75 ppm corresponding to the CH_3 protons which originally absorbed at 2.11 ppm, and a band centered at δ 7.4 ppm arising from the aromatic protons. The latter coincides with that observed in the original olefin. This assignment was confirmed by integration. During the course of the reaction the sum of both types of CH_3 protons remained in a constant ratio to the sum of the aromatic protons, and a similar relation held for the protons associated with the β carbon. The conversion of α-methylstyrene to the nitro compound is, therefore, quantitative.

Further evidence for the formation of carbonium ions in the reaction of tetranitromethane with olefins comes from studies of polymerization of oxetane initiated by this system. This cyclic ether is readily polymerized by cationic initiators but not by tetranitromethane alone. For example, no polymerization takes place in the system containing 1 *M* oxetane and 0.1 *M* tetranitromethane in nitrobenzene. On the other hand, polymerization of oxetane ensues when 1,1-diphenylethylene is added to the mixture of the ether and tetranitromethane in nitrobenzene. Obviously the intermediate carbonium ions formed in this system by the NO_2^+ transfer are responsible for the polymerization.

The transfer of NO_2^+ to the β-carbon atom of olefin, as shown in eq 2, is amply demonstrated. On the other hand, the transfer to aromatic rings does not take place. This was proved by the absence of polymerization when biphenyl, anthracene, or benzophenone (1 *M*) was added to the solution of oxetane (1 *M*) and tetranitromethane (0.1 *M*) in nitrobenzene.

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Effect of Solvation on the Reactivity of Ion Pairs

Sir:

At least two types of growing species, *viz.* ion pairs and free ions, participate in anionic polymerization carried out in certain ethereal solvents.[1-7] Furthermore, recent investigations[2,3] revealed that two types of ion pairs may contribute to propagation: the relatively inert contact pairs and the highly reactive solvent-separated pairs.

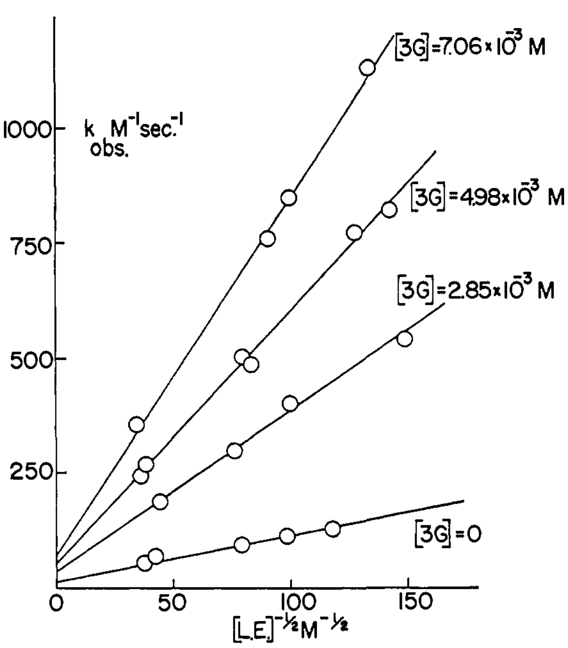

Figure 1. Linear dependence of propagation constant, k_{obsd}, of $\sim\!\sim S^-,Na^+$ polymerization on $1/[LP]^{1/2}$ at various concentrations of triglyme, 3G: solvent tetrahydropyran, 25°.

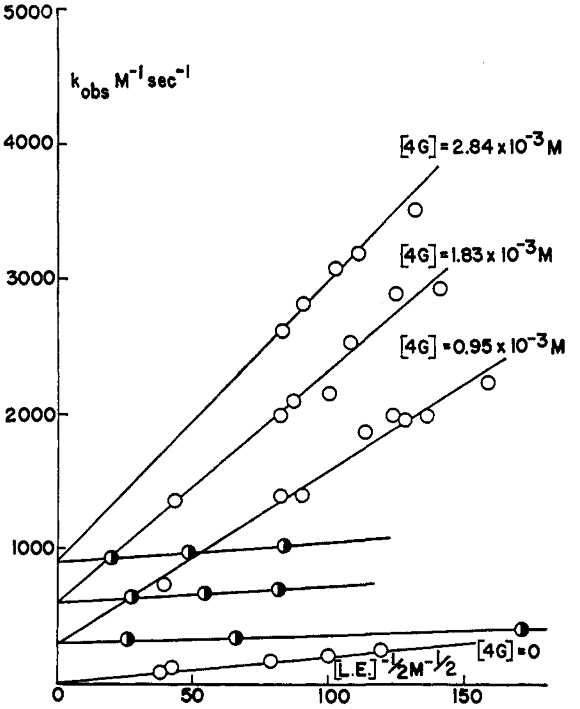

Figure 2. Linear dependence of propagation constant, k_{obsd}, of $\sim\!\sim S^-,Na^+$ polymerization on $1/[LP]^{1/2}$: solvent tetrahydropyran, 25°, in the absence and presence of tetraglyme. The half-shadowed points represent experiments performed in the presence of Na^+, BPh_4^- which depresses the ionic dissociation of the living polymer and thus facilitates the determination of the intercept.

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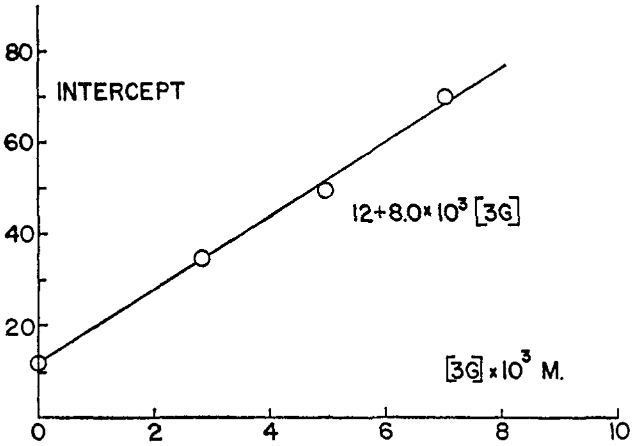

Figure 3. Plot of the intercept *vs.* [triglyme] from the results shown in Figure 1.

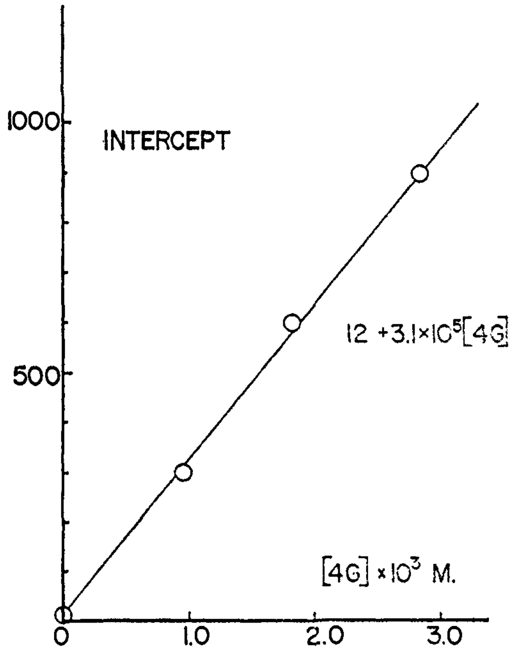

Figure 4. Plot of the intercept *vs.* [tetraglyme] from the results shown in Figure 2.

Our present study has shown that the sodium polystyryl ion pairs coordinate with suitable solvating agents (tri- or tetraglyme) and yield very reactive agent-separated pairs. Their formation affects the rate of propagation in two ways: (1) the contribution of ion pairs increases because of the presence of the reactive agent-separated pairs; (2) the contribution of the free ions becomes more significant because the coordination of the free Na^+ cations with the solvating agent increases the degree of dissociation of the ion pairs.

These effects were demonstrated by adding triglyme or tetraglyme to solutions of sodium polystyryl in tetrahydropyran at 25°. In the absence of glyme the observed propagation constant, k_{obsd}, is a linear function of the reciprocal of the square root of concentration of living polymers, *i.e.*

$$k_{obsd} = k'_{(\pm)} + k_{(-)}K_{diss}^{1/2}/[LP]^{1/2}$$

Here [LP] is the concentration of living polymers, $k'_{(\pm)}$ denotes the propagation constant of the ordinary pairs (probably of contact type), $k_{(-)}$ is the propagation constant of the free polystyryl ions, and K_{diss} is the equilibrium constant of the dissociation

$$\sim\!\sim S^-,Na^+ \rightleftharpoons \sim\!\sim S^- + Na^+ \qquad K_{diss}$$

This relation is demonstrated by the bottom lines in Figures 1 and 2 (drawn in different scales). In the presence of glyme two additional equilibria are established[8]

$$\sim\!\sim S^-,Na^+ + n\ \text{glymes} \rightleftharpoons \sim\!\sim S^-,(\text{glyme})_nNa^+ \qquad K_p$$

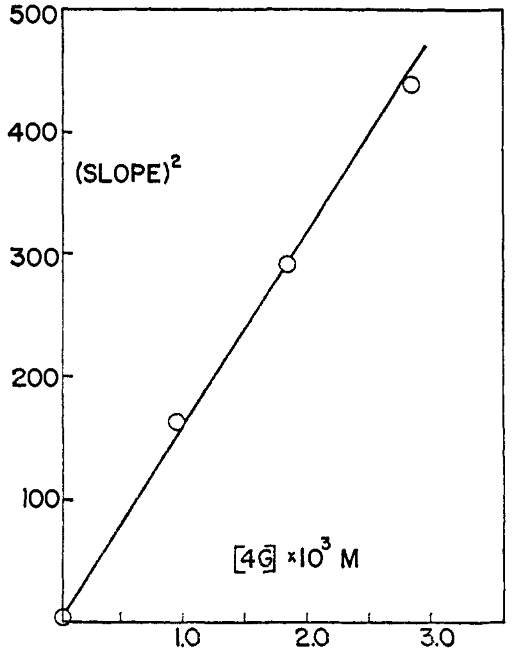

Figure 5. Plot of $(S_g^2 - S_0^2)$ *vs.* [tetraglyme] from the results shown in Figure 2.

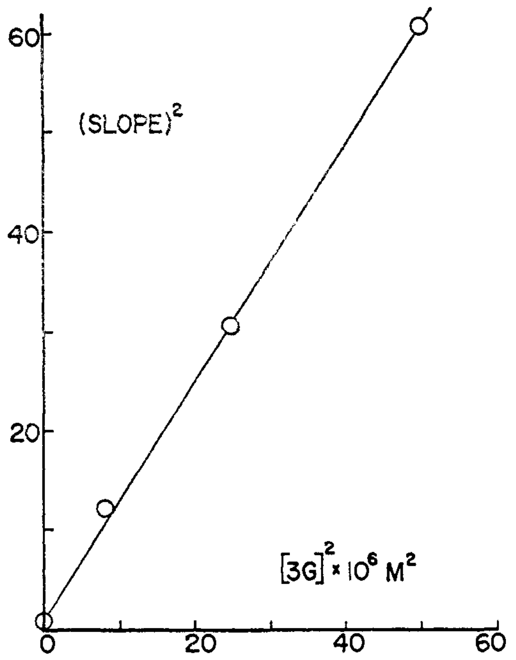

Figure 6. Plot of $(S_g^2 - S_0^2)$ *vs.* [triglyme]² from the results shown in Figure 1.

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[8] In a more general case each of these solvations may involve several equilibria, $n = 1, 2, \ldots$ and $m = 1, 2, \ldots$. We shall show that only one of them is significant for each system.

and

$$\text{Na}^+ + m\ \text{glymes} \rightleftharpoons \text{Na}^+(\text{glyme})_m \qquad K_i$$

Consequently

$$k_{\text{obsd}} = \{k'_{(\pm)} + k''_{(\pm)}K_p[\text{glyme}]^n\} + \{k_{(-)}K_{\text{diss}}^{1/2}(1 + K_i[\text{glyme}]^m)^{1/2}\}/[\text{LP}]^{1/2}$$

where $k''_{(\pm)}$ is the propagation constant of the agent-separated pair. The validity of the above equation hinges on the condition that 90% or more of living polymers remain in the form of ordinary $\sim\!\!\sim\text{S}^-,\text{Na}^+$ ion pairs. *A posteriori* calculations prove this to be the case in all our experiments.

We conclude, therefore, that the linear dependence of k_{obsd} *vs.* $1/[\text{LP}]^{1/2}$ is preserved in the presence of constant concentration of glyme, *i.e.*

$$k_{\text{obsd}} = I_g + S_g/[\text{LP}]^{1/2}$$

but the intercepts, I_g, and the slopes, S_g, are functions of the glyme concentration, and both increase with increasing [glyme]. This conclusion is verified, as seen in Figures 1 and 2.

To determine n and m, log $(I_g - I_0)$ and log $(S_g^2 - S_0^2)$ were plotted *vs.* log [glyme]. I_0 and S_0 refer to the intercept and slope, respectively, found in the absence of glyme. The plots are linear, the slopes being unity for all but the log $(S_g^2 - S_0^2)$ *vs.* log [glyme] obtained for triglyme, the latter having a value of 2. Hence, $n = 1$ for both glymes, while $m = 1$ for tetraglyme and 2 for triglyme.

These relations are verified by plotting I_g *vs.* [glyme]. The respective plots are shown in Figures 3 and 4. Both are linear, their slopes giving the product $k''_{(\pm)}K_p$, *viz.* $8 \times 10^3\ M^{-2}\ \text{sec}^{-1}$ for triglyme and $300 \times 10^3\ M^{-2}\ \text{sec}^{-1}$ for tetraglyme. Assuming that all solvent- or agent-separated sodium polystyryl pairs propagate with virtually the same rate constant of $20{,}000\ M^{-1}\ \text{sec}^{-1}$ (see ref 2 and 3), we calculate K_p to be $0.4\ M^{-1}$ for triglyme and $15\ M^{-1}$ for tetraglyme; *i.e.*, the latter coordinates with $\sim\!\!\sim\text{S}^-,\text{Na}^+$ about 40 times more powerfully than the former.

Similarly, plots of S_g^2 *vs.* [tetraglyme] and [triglyme]^2 are linear, as shown in Figures 5 and 6. The slopes give $K_i = 1.6 \times 10^5\ M^{-1}$ for tetraglyme and $1.2 \times 10^5\ M^{-2}$ for triglyme.

The spectacular effects of tetraglyme are revealed by Figure 2. At $[\text{LP}] = 5 \times 10^{-5}\ M$, tetraglyme at concentration lower than $3 \times 10^{-3}\ M$ increased the rate of polymerization nearly by a factor of 200.

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Study of Ion-Molecule Reaction Mechanisms in Acetonitrile by Ion Cyclotron Resonance

Sir:

The ion-molecule chemistry of acetonitrile has been studied previously by high-pressure mass spectrometry.[1-3] Reactions 1 and 2 were identified through examination of the mass spectra as functions of pressure and time.[3]

$$\text{CH}_3\text{CN}^+ + \text{CH}_3\text{CN} \longrightarrow \text{CH}_4\text{CN}^+ + \text{CH}_2\text{CN} \qquad (1)$$

$$\text{CH}_2\text{CN}^+ + \text{CH}_3\text{CN} \longrightarrow \text{C}_2\text{H}_4\text{CN}^+ + \text{HCN} \qquad (2)$$

Reactions 3–5 were also mentioned as probable.

$$\text{CH}_2\text{CN}^+ + \text{CH}_3\text{CN} \longrightarrow \text{CH}_4\text{CN}^+ + \text{CHCN} \qquad (3)$$

$$\text{CH}_4\text{CN}^+ + \text{CH}_3\text{CN} \longrightarrow \text{H}(\text{CH}_3\text{CN})_2^+ \qquad (4)$$

$$\text{CH}_4\text{CN}^+ + \text{CH}_3\text{CN} \longrightarrow \text{CH}_3^+ + \text{HCN} + \text{CH}_3\text{CN} \qquad (5)$$

Since acetonitrile is one of a group of small molecules important in theories of abiogenic synthesis in primitive atmospheres,[4-6] and since ion-molecule reactions may be relevant in the assignment of biochemically important reaction pathways, it is of interest to reexamine this chemistry by ion cyclotron resonance spectroscopy (icr).

The icr spectra in this study were obtained using the Varian ion cyclotron resonance spectrometer. The basic description of the spectrometer and the application of single and double resonance have appeared previously.[7-10] Icr single resonance spectra are very similar to ordinary mass spectra yet still permit ion-molecule reaction products to be easily observed. Consider the reaction to be $\text{A}^+ + \text{B} \rightarrow \text{C}^+ + \text{D}$. By using pulsed double resonance and phase-sensitive detection, the signal from C^+ can be continuously monitored while an irradiating radiofrequency field is swept through a range of cyclotron frequencies. When the irradiating frequency matches the natural cyclotron frequency of A^+, energy is absorbed by A^+ from the irradiating field and its translational energy is increased. Since most reaction rate constants are energy dependent, the population of C^+ will change, and this change is presented as a peak in the double-resonance spectrum. This will occur for all ions which give C^+ as a product if the irradiating frequency is swept through the cyclotron frequencies of all of the ions. This experiment can be done for any ion so that the entire ion-molecule chemistry can be mapped out.

Figure 1 shows the single resonance icr spectrum of acetonitrile. Utilizing the technique described above, the ion-molecule reactions listed in Table I were identified. Reactions 1, 2, 4, and 5 of Table I were reported by Franklin, *et al.*,[3] but in our studies the reaction of CH_4CN^+ and CH_3CN to give CH_3^+, HCN, and CH_3CN was not found. Indeed, the only reaction involving these species is reaction 13 in Table I where CH_3^+ serves as a proton donor to neutral acetonitrile.

As an example of the versatility of icr, further studies on reaction 4 were conducted. In place of acetonitrile of natural isotopic abundance, two different mixtures were examined, one of approximately 1:1 $\text{CH}_3\text{CN}:\text{CD}_3\text{CN}$ and another of 4:1 $\text{CH}_3\text{C}^{14}\text{N}$:

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