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Anionic Polymerization of Styrene in Binary Solvents

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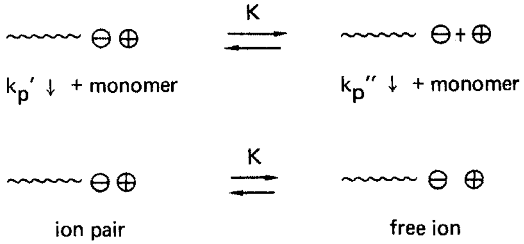
ABSTRACT

Experimental findings on the triple ion formation were examined by adopting more elaborate purification method for solvents. For polystyryllithium in dimethoxyethane (DME) and benzene mixtures, the overall rate constant of propagation (k_p) was confirmed to <u>increase</u> with increasing living end concentration under some conditions, in contrast with cases for polystyryllithium in tetrahydrofuran-benzene mixtures and for polystyryl sodium, potassium and cesium in DME-benzene mixtures. The propagation by the intermolecular triple ions proposed earlier in order to elucidate the kinetic "anomaly" mentioned above was briefly discussed.

It had been firmly established by the pioneering work of Szwarc and Schulz on the kinetics of living anionic polymerizations of styrene in ethereal solvents that the propagation proceeds through two types of the growing chain ends, namely free ions and ion pairs [1]:



If one denotes the dissociation constant by K and the propagation rate constants of the ion pairs and of the free ions by k_p' and k_p'', respectively, the mass action law gives the following equation for the overall rate constant of propagation k_p:

$$k_p = k_p' + k_p'' K^{1/2} [LE]^{-1/2} \tag{1}$$

where [LE] is the concentration of the growing chain ends. It has been demonstrated that Eq. (1) holds for a variety of living anionic systems. The binary solvent systems have not been exceptions. Figure 1 shows one of the examples obtained for polystyryllithium in tetrahydrofuran (THF)-benzene mixtures [2]. Clearly the intercept of the k_p-$[LE]^{-1/2}$ plot is k_p' and the slope is $k_p'' K^{1/2}$. Because these constants have definite physical significances, the intercept and slope under consideration should be positive. This has usually been the case.

In continuation of our research project, we studied binary solvent mixtures of dimethoxyethane (DME) and benzene for polystyryllithium [3] in order to compare their behavior with that in THF-benzene mixtures studied earlier [2]. The DME-benzene mixtures showed unexpectedly anomalous behavior in the kinetic pattern, as is shown in Fig. 2. At low concentrations of DME and at high concentrations of the growing chain ends, the k_p value <u>increased</u> with decreasing $[LE]^{-1/2}$. If a linear approximation is allowed, the slope is negative (instead of positive), which is physically impossible. This anomaly was attributed in the previous study [3] to formation of the intermolecular triple ions. At the same time, however, it was also inferred that another

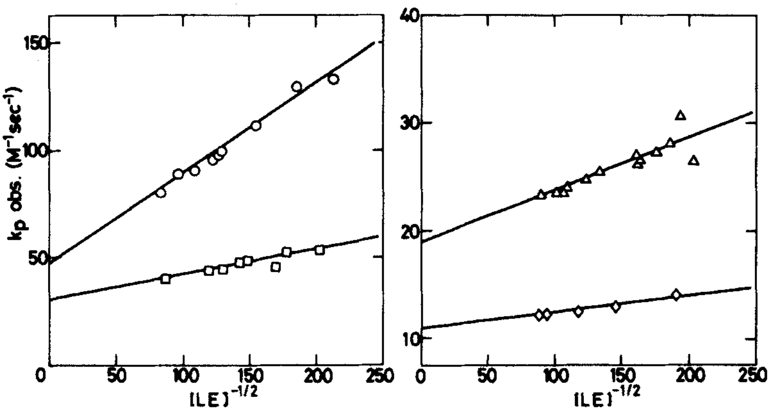


FIG. 1. Dependence of the apparent propagation constant on polystyryllithium concentration in THF-benzene mixtures at 25°C. THF contents in percent: (○) 60; (□) 50; (△) 40; and (◇) 30.

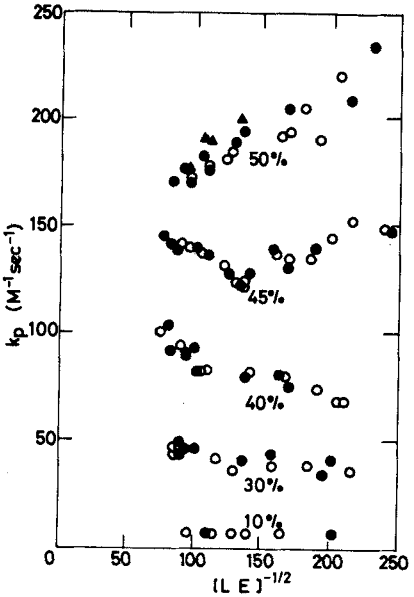


FIG. 2. Dependence of the apparent propagation constant on polystyryllithium concentration in DME-benzene mixtures at 25°C. The DME contents are given as percentages in the figure. The filled and open symbols indicate data obtained by independent runs at 5(▲), 3(●), and 0(○) kV/cm.

factor or other factors were responsible for the observed deviation from the two-state mechanism. The most serious case is the possible contribution of impurities which could not be removed from the polymerization systems by our previous purification methods. Thus it was intended to examine the purification procedures and to find a better method for purification. After almost 4 years of trial and error processes, we finally managed to arrive at a "new" purification method [4] which is compared with the old one in Table 1. The important points in the new purification method are the argon gas and the repeated drying-deaeration cycles. According to the manufacturer, the argon contained a smaller amount of oxygen than the nitrogen. We suspected that the oxygen might have a vitiating effect to the kinetic data. Furthermore, the deaeration-drying cycle in the previous method was broken when the solvent (DME or THF) started showing a dark blue color. In the revised procedure, this criterion was abandoned and the cycle was further continued until bubbling, which could be noticed when the stoppers of the vacuum line were opened instantaneously, became weak and constant.

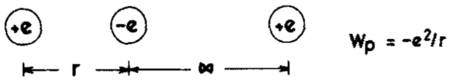
TABLE 1. Purification Methods of Solvents

Step	In 1970	In 1974
1	Solvents were dried over Na for:	
	1 week	1 month
2	Dried solvents were refluxed over CaH_2 and distilled off into a vessel into which Na-K alloy was introduced under an atmosphere of:	
	Nitrogen (O_2: 0.005%)	Argon (O_2: 0.0005%)
3	The glass vessels were connected with a vacuum line and cooled down to -78°C, and the stopper was opened instantaneously to deaerate the solvent and closed again. The cycle was repeated:	
	Until dark blue color developed	For about 3 weeks until degassing became weak and constant

By using such a more elaborate purification procedure, the observed kinetic data became slightly larger. For example, at 25°C and a DME content of 40% for polystyryllithium, k_p'' is 5.1×10^4 $M^{-1}sec^{-1}$ in the 1974 work whereas it was 2.7×10^4 $M^{-1}sec^{-1}$ in the 1971 work. The k_p' became larger from 32 $M^{-1}sec^{-1}$ to 68 $M^{-1}sec^{-1}$. At a DME content of 50%, k_p' is 87 $M^{-1}sec^{-1}$ whereas it was 78 $M^{-1}sec^{-1}$, and k_p'' is 5.4×10^4 $M^{-1}sec^{-1}$ where it was 3.3×10^4 $M^{-1}sec^{-1}$ [5]. In spite of such a numerical discrepancy, the basic feature of the concentration dependence of k_p was not essentially affected; that is, k_p increased with an increasing concentration of living ends at low DME contents, or the Szwarc-Schulz plots again showed a negative slope as was found in the 1971 work.

Thus it seems that the triple ion contribution is highly possible. According to the electrochemistry, not only free ions and ion-pairs, but also higher ionic aggregates can exist in weak electrolyte solutions, especially in low dielectric media. If the dielectric constant is lowered, triple ions are formed in addition to free ions and ion-pairs. If the dielectric constant is further lowered, quadruples may be formed. The consideration of the potential energy of a system containing three ions makes understanding easier:

Ion Pair



Triple Ion

Suppose that we have two oppositely charged ions and one positively charged ion, all having equal size. If the first two are separated by a distance r and the third by infinity (or if an ion-pair is formed), the potential energy is $W_p = -e^2/r$. If the three ions are separated from each other by r from the nearest neighbor (or if a triple ion is formed), the potential energy of the system is $W_t = -3e^2/2r$. The triple ions are more stable than the ion-pairs.

Next we want to discuss the conductance equation by Fuoss and Kraus [6] for solutions containing free ions, ion-pairs, and triple ions. In this case we have three dissociation equilibria,

$$AB \rightleftarrows A^+ + B^- \qquad K \tag{2}$$

$$(A_2B)^+ \rightleftarrows A^+ + AB \qquad k_1 \tag{3}$$

$$(AB_2)^- \rightleftarrows AB + B^- \qquad k_2 \tag{4}$$

the respective dissociation constants being K, k_1, and k_2. If we assume $k_1 = k_2 = k$, or, in other words, if we assume bilateral triple ion formation with the same stability, the mass action law gives

$$1 - \gamma - 3\gamma_3 = C\gamma^2K^{-1} \qquad \text{for ion-pairs} \tag{5}$$

and

$$C\gamma(1 - \gamma - 3\gamma_3) = \gamma_3 k \qquad \text{for triple ions} \tag{6}$$

where C is the electrolyte concentration, and γ and γ_3 are the fractions of free ions and ion-pairs, respectively. For low dielectric media, we can assume that γ and γ_3 are much smaller than unity. Then we have

$$\gamma = (C/K)^{-1/2} \tag{7}$$

and

$$\gamma_3 = (CK)^{1/2}k^{-1} \tag{8}$$

Since the total conductance Λ is the sum of the conductances of the free ions and triple ions, we have

$$\Lambda(= \gamma\Lambda_0 + \gamma_3\lambda_0) = \Lambda_0K^{1/2}C^{-1/2} + \lambda_0K^{1/2}C^{1/2}k^{-1} \tag{9}$$

where Λ_0 is the sum of the limiting conductances of free cations and anions, and λ_0 the sum of the conductances of free ions and triple ions. At lower concentration, Eq. (9) reduces to

$$\Lambda = \Lambda_0 K^{1/2} C^{-1/2} \tag{10}$$

whereas at higher concentrations it simplifies to

$$\Lambda = \lambda_0 K^{1/2} k^{-1} C^{1/2} \tag{11}$$

In other words, Λ decreases at first with increasing concentration, and then increases through a minimum at a concentration $C_{\min}$. From Eq. (9) we have

$$C_{\min} = k\Lambda_0/\lambda_0$$

and the conductance at $C_{\min}$, $\Lambda_{\min}$, is given by

$$\Lambda_{\min} = 2(\gamma\Lambda_0)_{\min} = 2(\gamma_3\lambda_0)_{\min}$$

In other words, the conductance of the triple ions is equal to that of the free ions at this concentration.

The situation is well understood by Fuoss and Kraus data for tetraisoamylammonium nitrate in H_2O-dioxane mixtures [6], which are shown in Table 2. With increasing concentration, the fraction of free ions (γ) decreases whereas that of triple ions (γ_3) increases. The observed conductance, which is in good agreement with the value calculated by Eq. (9), decreases and increases after passing a minimum. At $C = 8.0 \times 10^{-5}$, the fractions of the free ions and of the triple ions are equal. At $C = 24 \times 10^{-5}$, the conductance shows a minimum. An important point is that the triple ion contribution cannot be overlooked even in the concentration range below $C_{\min}$, where the conductance decreases with increasing concentration.

In this respect it is interesting to examine the concentration dependence of the electric conductance of the living polymer systems. As shown in Fig. 3, log Λ decreases linearly with log[LE] [4]. The slopes of the linear relationship, summarized in Table 3, are smaller than +0.5. These values are, however,

TABLE 2. Comparison of γ and γ_3

$C \times 10^5$ (M)	$\gamma \times 10^5$	$\gamma_3 \times 10^5$	$\Lambda \times 10^4$	
			Calc	Obs
1.5	2.4	0.5	7.7	7.5
3.0	1.7	0.7	5.8	5.8
8.0	1.1	1.1	4.4	-
10	0.95	1.2	4.05	4.03
24	0.61	1.9	3.68	-
30	0.55	2.1	3.75	3.68
100	0.30	3.8	4.70	5.25

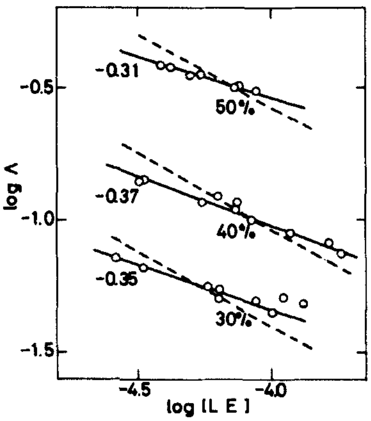


FIG. 3. Dependence of the equivalent conductance Λ on the living end concentration in DME-benzene mixtures at 0°C.

definitely larger than -0.5 which is indicated in Fig. 3 by dashed lines. The deviation from -0.5 implies that the polymerization systems studied are in an intermediate state between those which can be described by Eq. (10) and by Eq. (11), respectively. In other

TABLE 3. Slope Values of the log Λ-log[LE] Plots for Polystyryllithium in DME-Benzene Mixtures [4]

DME content (%)	Temperature (°C)	Slope
30	0	-0.3_5
40	0	-0.3_7
	25	-0.4_0
	35	-0.4_4
50	0	-0.3_1
	25	-0.4_6

words, there exist not only free ions and ion-pairs, but also triple ions in the polymerization systems.

It should be noted that the previous work [2] also gave slope values for log Λ-log[LE] plots larger than -0.5.

For justification of the presence of the triple ions, the following consideration would be useful. First, the Fuoss-Kraus theory [7] showed that the critical concentration (C_0), at which the free ion—ion-pair equilibrium starts to fail completely, can be given by

$$C_0 = 3.2 \times 10^{-7} D^3 \qquad (12)$$

for 1-1 electrolytes and 25°C, where D is the dielectric constant. The C_0 values for the DME-benzene mixtures were found to be 2.6×10^{-5}, 2.2×10^{-5}, and 1.8×10^{-5} M for DME contents of 50, 45, and 40%, respectively. It is to be noted that almost all of our kinetic measurements were carried out at higher concentrations (2×10^{-5} to 2×10^{-4}) than these C_0 values. Second, it is interesting to compare C_{min} and the concentrations employed in the kinetic study. Since the mobility of the gegenions (Li^+ in the present case) is expected to be larger than those of bulky polystyryl free ions and triple ions, we can assume $\Lambda_0 \approx \lambda_0$. Then $C_{min} \approx k$. The dissociation constants k determined from the conductance data (and hence the

C_{min} values) are 6.7×10^{-5}, 1.8×10^{-4}, and 4.8×10^{-4} M at 0°C for DME contents of 30, 40, and 50%, respectively. It is to be remembered that the kinetic and conductance measurements were mostly carried out in a concentration range below these C_{min} values. Thus we may expect Λ to decrease with increasing concentration, even when we have triple ions in addition to free ions and ion-pairs.

The next question is the structure of the triple ions in the living anionic systems. Naturally, we have two possibilities; $\oplus\ominus\oplus$ and $\ominus\oplus\ominus$. Because the negative charge is located at the end of the growing chains, it would not be easy to accept that the triple ion $\oplus\ominus\oplus$ is stable. Furthermore, if it exists, its reactivity would be expected to be smaller than that of ion-pairs (both solvent-separated or contact). The observed fact, however, is the argumentation of the overall rate constant (k_p) with increasing living end concentration. Thus we may exclude the contribution of the triple ions $\oplus\ominus\oplus$.

If the above argument is acceptable, we have only $\ominus\oplus\ominus$ triple ions; in other words, the triple ion formation is unilateral [8]. Then, if precise data analysis is our aim, Eq. (9) cannot be applied to the present living anionic systems because this equation was derived for bilateral triple ion systems. Thus we have to use Wooster's equation for unilateral systems, which reads

$$\Lambda\left(1 + \frac{C}{k}\right)^{1/2} = \Lambda_0K^{1/2}C^{-1/2} + \lambda_0K^{1/2}k^{-1}C^{1/2} \qquad (13)$$

This equation can be rearranged into

$$C\Lambda^2 = \Lambda_0^2K + (2\Lambda_0\lambda_0 - \Lambda_0^2)(K/k)C \qquad (14)$$

which shows that $C\Lambda^2$ is a linear function of C. The conductance data [4] of polystyryllithium in DME-benzene mixtures are shown in Fig. 4 according to Eq. (14). As expected, the plot gives linear relationships. From the slope and intercept, the K and k values are estimated using the conductance values, which are determined by the Walden product, and by the assumption that $\Lambda_0 = \lambda_0$.

When the propagation process proceeds through the three-state mechanism, namely by free ions, ion-pairs, and triple ions, the

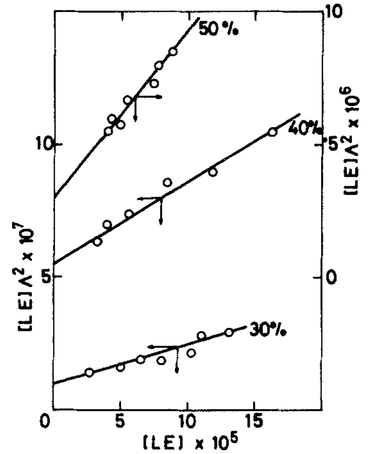


FIG. 4. Wooster plot for triple ion formation of polystyryllithium in DME-benzene mixtures at 0° [4].

overall rate constant (k_p) is a function of k_p', k_p'', and k_p''' (the rate constant of the triple ions):

$$k_p = (1 - \gamma - 2\gamma_3)k_p' + \gamma k_p'' + \gamma_3 k_p''' \tag{15}$$

In nonpolar solvents, such as those used in our study, we may assume $\gamma \ll 1$ and $\gamma_3 \ll 1$. Thus we have

$$\begin{aligned} k_p = {} & k_p' + k_p''K^{1/2}\left(1 + \frac{[LE]}{k}\right)^{-1/2}[LE]^{-1/2} \\ & + k_p'''K^{1/2}\left(1 + \frac{[LE]}{k}\right)^{-1/2}k^{-1}[LE]^{1/2} \end{aligned} \tag{16}$$

Obviously, k_p is a fairly complicated function of the living end concentration. In other words, k_p is not generally a linear function of $[LE]^{1/2}$ or of $[LE]^{-1/2}$. Thus the graphical method employed by Szwarc and Schulz [1] for determination of the rate constants cannot be applied. Furthermore, to be exact, it is not allowed to draw a straight line in the k_p-$[LE]^{-1/2}$ plot such as is shown in Fig. 2.

Thus we have to employ a numerical calculation method in order to estimate k_p', k_p'', and k_p''' as follows.

First, Eq. (16) was expanded in series of [LE]/k:

$$k_p = k_p' + K^{1/2}k_p''[LE]^{-1/2} + K^{1/2}\left(k_p''' - \frac{k_p''}{2}\right)k^{-1}[LE]^{1/2} + \cdots \qquad (17)$$

A first approximation of k_p''' was substituted into Eq. (17), which was roughly estimated by a "linear" approximation for the k_p-$[LE]^{1/2}$ plot [11]. Then $k_p - K^{1/2}k^{-1}(k_p''' - \frac{1}{2}k_p'')[LE]^{1/2}$ was plotted against $[LE]^{-1/2}$ to obtain a second approximation for k_p''. In this plot, $\frac{1}{2}k_p''$ was estimated by using the first approximation for k_p'', which was obtained from the "positive" slope of Fig. 2, when possible. The $[k_p - K^{1/2}k_p''[LE]^{-1/2}]$ was plotted against $[LE]^{1/2}$ by using the second approximation of k_p'' to evaluate a second approximation for k_p'''. This k_p''' value was used for a third approximation for k_p'', which was further recycled for higher approximations for k_p'' and k_p'''. The calculation cycle was continued until k_p'' and k_p''' became constant. The final results thus obtained are compiled in Table 4.

It should be reminded that, for polystyryllithium in THF-benzene mixtures, the k_p-$[LE]^{-1/2}$ plot gave quite a normal behavior as shown in Fig. 1. Likewise, polystyryl sodium, potassium, and cesium demonstrated the usual kinetic pattern [12]. The anomalous behavior was originally found [3] and subsequently confirmed [4] exclusively for polystyryllithium in DME-benzene mixtures. Consequently, we would like to confirm our previous claim that the triple ions in the present system are formed as a consequence of the molecular geometry of DME and of its solvating power which is specific to lithium ions, probably because of the small Pauling radius. Furthermore, the triple ions under consideration are of the solvent-separated intermolecular type, and, for this reason, their reactivity (k_p''') is larger than that of the free ions (see Table 4 [13], as was pointed out earlier [3].

TABLE 4. Dissociation and Reactivity of Lithium Salts of Living Polystyrene in Dimethoxyethane and Benzene Mixtures [4]

DME content (%)	Temperature (°C)	D	Λ_0 (cm^{2}ohm^{-1} equiv^{-1})	K × 10^{10} (M)	k × 10^4 (M)	k_p' (M^{-1} sec^{-1})	k_p'' × 10^{-4} (M^{-1} sec^{-1})	k_p''' × 10^{-4} (M^{-1} sec^{-1})
30	0	3.60	36.2	0.76	0.67	15	2.1	4.5
40	0	4.07	37.7	3.9	1.8	40	2.1	6.5
	25	3.81	57.7	0.43	2.0	68	5.1	10
	35	3.70	68.0	0.15	2.3	80	7.6	13
50	0	4.67	39.3	19	4.8	120	2.2	7.4
	25	4.33	59.5	2.5	5.1	87	5.4	11

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The present work was accomplished by painstaking efforts of H. Hirohara, T. Makino, K. Takaya, M. Nakayama, H. Tatsuta, and H. Yamauchi.

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[3] N. Ise, H. Hirohara, T. Makino, K. Takaya, and M. Nakayama, *Ibid.*, 74, 606 (1970).

[4] K. Takaya and N. Ise, *J. Chem. Soc., Faraday I*, 74, 1338 (1974).

[5] The disagreement is disturbing. However, it is to be noted that k_p' and k_p'' for other systems also became much larger. We know the deep grief of Macbeth who said long ago, "All our yesterdays have lighted fools the way to dusty death."

[6] R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, 55, 2387 (1933).

[7] R. M. Fuoss and F. Accascina, *Electrolytic Conductance*, Interscience, New York, 1959, Chap. 18.

[8] The term "unilateral" was first coined by Wooster thirty-seven years ago [9]. This author discussed monosodium benzophenone in liquid ammonia, which formed negatively charged triple ions. Though this unilateral triple ion is due to a chemical bond, he correctly pointed out [10] that "coulombic forces alone might give rise to a situation which closely simulates unilateral triple ion formation . . ., if one of the simple ions is much larger than the other . . . ." He also analyzed the triple ion formation in aqueous hydrofluoric acid solutions.

[9] C. B. Wooster, *J. Amer. Chem. Soc.*, 59, 377 (1937).

[10] C. B. Wooster, *Ibid.*, 60, 1609 (1938).

[11] Under some conditions, Eq. (15) reduces to a much simpler form. First, if [LE]/k is smaller than unity, we have

$$k_p = k_p{}' + k_p{}''K^{1/2}[LE]^{-1/2} + k_p{}'''K^{1/2}k^{-1}[LE]^{1/2} \tag{A}$$

If $k_p{}''$ is large or k is large, the third term of the left-hand side of Eq. (A) can be ignored and we have

$$k_p = k_p{}' + k_p{}''K^{1/2}[LE]^{-1/2} \tag{B}$$

which is nothing else than Eq. (1). Obviously, the case considered by Szwarc and Schulz [1] is a limiting one of Eq. (16). Furthermore, if $k_p{}'''$ is large or if k is small, we may have

$$k_p = k_p{}' + k_p{}'''K^{1/2}k^{-1}[LE]^{1/2} \tag{C}$$

In other words, if the triple ion contribution is overwhelming, $k_p{}'$ is a linear function of $[LE]^{1/2}$. The kinetic data for the polystyryllithium in DME-benzene mixtures under consideration showed that k_p was very approximately a linear function of $[LE]^{1/2}$. From this linear approximation, the first approximation of $k_p{}'''$ was conveniently evaluated and introduced into the numerical calculation mentioned in the text.

Concerning Eq. (1), it should be emphasized, the two-state mechanism leads us to Eq. (1) but the linearity between k_p and $[LE]^{-1/2}$ does not necessarily imply that there exist only free ions and ion pairs. Even if we have concurrently the free ions, ion pairs, and triple ions, the observed rate equation apparently becomes identical to Eq. (1) when the triple ions happen to have a low reactivity.

[12] K. Takaya, S. Yamauchi, and N. Ise, J. Chem. Soc., Faraday I, 74, 1330 (1974).

[13] As pointed out in the text, the triple ions are more reactive than the free ions. We are not claiming, however, that this is always the case. The triple ions of a contact type, if they exist, should be less reactive than the free ions. The reactivity of various kinds of growing ends is expected to depend sensitively on their solvation. Naturally, nonsolvated free ions should be most reactive.