Stopped-Flow Study of the Cationic Polymerization of Styrene Derivatives. 2.[1] Solvent Effect on the Polymerization of *p*-Methoxystyrene. Evidence for the Multiplicity of the Propagating Species

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ABSTRACT: A stopped-flow study of solvent effects on the cationic polymerization of *p*-methoxystyrene has presented evidence for the multiplicity of the propagating species. Propagation rate constants (k_p) for four initiators (CH_3SO_3H, iodine, $BF_3 \cdot O(C_2H_5)_2$, and $SnCl_4$) were determined from the intermediate absorption at 380 nm in 1,2-dichloroethane/carbon tetrachloride mixtures at 30 °C. The k_p values for CH_3SO_3H and iodine steadily increased with decreasing solvent polarity, whereas those for the metal halides remained almost unchanged. The former unusual trend was explained by involvement of an "invisible" propagating species that has no absorption in the UV–visible region and becomes prodominant in less polar media. The small solvent effect on the k_p values for the metal halides suggested that the propagating species (with the 380-nm band) derived from these initiators have a similar reactivity in both polar and nonpolar solvents. Absorption spectra recorded under preparative polymerization conditions ($[M]_0 = 0.10$ M) supported the existence of the "invisible" species, showing that CH_3SO_3H gave polymers in high yield even when no absorption was observed at 380 nm.

The propagating species in the cationic polymerization of *p*-methoxystyrene can be directly observed by stopped-flow spectroscopy. We have shown this in our recent work,[1] in which an intermediate absorption detected at 380 nm in 1,2-dichloroethane ($(CH_2Cl)_2$) has been assigned to the propagating carbocation. Quantitative spectroscopic data gave its propagation rate constants (k_p) for a variety of initiators (CH_3SO_3H, iodine, $BF_3 \cdot O(C_2H_5)_2$, and $SnCl_4$). The independence of k_p values on the initiators indicated that in $(CH_2Cl)_2$, a polar solvent, the nature of the propagating species little depends on counterion structure, and involvement of a free ionic species was suggested.

For a further insight into the nature of the propagating species, the present work extends our stopped-flow investigations to the *p*-methoxystyrene polymerization in less polar media, namely in $(CH_2Cl)_2/CCl_4$ solvent mixtures with various dielectric constants ranging from 5 to 10. Results of these spectroscopic measurements were also compared with those under preparative polymerization conditions (at a higher monomer concentration ($[M]_0$)). Evidence for the multiplicity of the propagating species was presented and discussed.

Experimental Section

Materials. *p*-Methoxystyrene was prepared as previously reported.[1,2] Solvent purification methods were also described elsewhere.[1] 1,2,3,4-Tetrahydronaphthalene as internal standard for gas chromatography was purified by distillation of a commercial product (guaranteed reagent) under reduced pressure.

Spectroscopic Measurement. Details of stopped-flow experiments ($[M]_0 = 5.0$ mM) were given in the previous paper.[1] Spectra of polymerization solutions at a higher $[M]_0$ (0.10 M) were recorded on a JASCO UVIDEC-1 double-beam spectrophotometer at room temperature (optical path length 1 cm). As reference was used a monomer solution (0.10 M) in the same solvent as in the polymerization.

Preparative Polymerizations. Polymerizations at $[M]_0 = 0.10$ M were performed in a flask equipped with a three-way cock under dry nitrogen at 30 °C. Several runs were done in a closed optical cell with a three-way cock to measure absorption spectra (see above). The reaction was stopped by adding ammoniacal methanol and monomer consumption was followed by gas chromatography. Product polymers were precipitated into an excess of methanol, filtered off, washed with methanol, and dried in vacuo. Their molecular weight distribution was determined by gel permeation chromatography as reported.[3]

Results and Discussion

Absorption Spectra. The polymerizations of *p*-methoxystyrene ($[M]_0 = 5.0$ mM) with four initiators (CH_3SO_3H, iodine, $BF_3 \cdot O(C_2H_5)_2$, and $SnCl_4$) were followed by stopped-flow spectroscopy in $(CH_2Cl)_2/CCl_4$ mixtures with various dielectric constants. Figures 1–3 show relevant absorption spectra of the reaction mixtures for the first three initiators. In each figure spectra recorded at the same polymerization time were compared. Results for $SnCl_4$ initiator were similar to those for $BF_3 \cdot O(C_2H_5)_2$ and the figure was omitted. In all the systems decreasing solvent polarity by addition of CCl_4 reduced the 380-nm peak due to the propagating species.[1] There appeared no other peak in the spectra; the intermediate peak neither shifted nor became broader, indicating that in both $(CH_2Cl)_2$ and its mixtures with CCl_4 the observed intermediate exhibits its absorption only at 380 nm.

In the following part of this study, CH_3SO_3H and $BF_3 \cdot O(C_2H_5)_2$ were mainly employed as initiators, because iodine and $SnCl_4$ gave similar results to those for CH_3SO_3H and $BF_3 \cdot O(C_2H_5)_2$, respectively.

The concentration of the propagating species ($[P^*]$) determined from the absorbance at 380 nm increased with time in a time scale of seconds and reached a maximal value ($[P^*]_{max}$) before decreasing gradually. Figure 4 illustrates changes in the $[P^*]_{max}$ values with solvent dielectric constant. It was assumed for determination of $[P^*]$ that the molar absorptivity (ϵ_{380}) of the 380-nm peak is solvent independent and equals 2.8×10^4 M^{-1} cm^{-1}.[1] $[P^*]_{max}$ generally decreased with decreasing solvent polarity, whereas with $BF_3 \cdot O(C_2H_5)_2$ initiator it appears to reach a constant value in sufficiently nonpolar media. In contrast, $[P^*]_{max}$ in the CH_3SO_3H system was continuously reduced nearly to zero as indicated by the very small value ($(6\text{–}9) \times 10^{-8}$ M) in a solvent containing 60 vol % CCl_4. $BF_3 \cdot O(C_2H_5)_2$ gave a much larger $[P^*]_{max}$ (ca. 2×10^{-6} M) in the same solvent.

Propagation Rate Constants. The monomer consumption rate was also followed (at 295 nm[1]) in less polar solvents, as shown by the first-order conversion curves in Figure 5. The rate decreased with decreasing solvent polarity in both the CH_3SO_3H and $BF_3 \cdot O(C_2H_5)_2$ systems. From these data k_p values were determined according to the following equation:[1]

$$\ln \frac{[M]_{t_1}}{[M]_{t_2}} = \frac{k_p}{\epsilon_{380}} \int_{t_1}^{t_2} \Delta OD_{380} \, dt \qquad (1)$$

where ΔOD_{380} is the absorbance at 380 nm. Plots of eq 1 gave straight lines through the origin in all cases. Table I lists the k_p values, as defined by eq 1, obtained in a variety of solvents,

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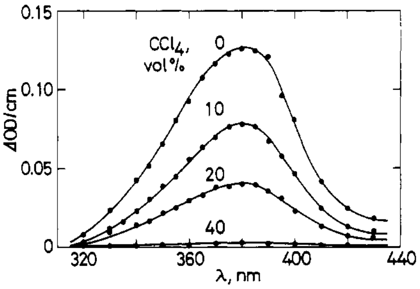

Figure 1. Absorption spectra of the *p*-methoxystyrene/CH_3SO_3H systems in $(CH_2Cl)_2/CCl_4$ mixtures at 30 °C: $t = 1.0$ s; $[M]_0 = 5.0$ mM; $[C]_0 = 5.0$ mM.

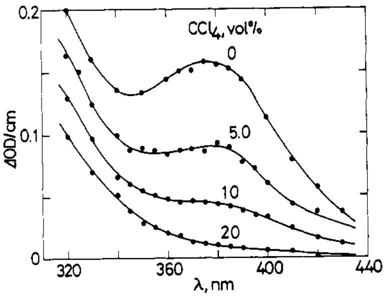

Figure 2. Absorption spectra of the *p*-methoxystyrene/iodine systems in $(CH_2Cl)_2/CCl_4$ mixtures at 30 °C: $t = 30$ s; $[M]_0 = 5.0$ mM; $[C]_0 = 5.0$ mM.

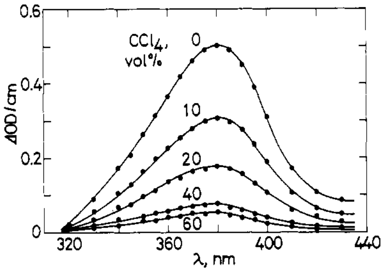

Figure 3. Absorption spectra of the *p*-methoxystyrene/$BF_3 \cdot O(C_2H_5)_2$ systems in $(CH_2Cl)_2/CCl_4$ mixtures at 30 °C: $t = 10$ s; $[M]_0 = 5.0$ mM; $[C]_0 = 0.50$ mM.

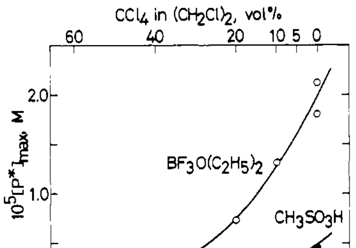

Figure 4. Dependence of the maximal concentration of the propagating species ($[P^*]_{max}$) on solvent dielectric constant at 30 °C: $[M]_0 = 5.0$ mM; $[C]_0$ (CH_3SO_3H) 5.0 mM, ($BF_3 \cdot O(C_2H_5)_2$) 0.50 mM.

and their dependence on solvent polarity is depicted in Figure 6 for CH_3SO_3H and $BF_3 \cdot O(C_2H_5)_2$. With the metal halides ($BF_3 \cdot O(C_2H_5)_2$ and $SnCl_4$) the k_p values varied little (or only slightly increased) with solvent polarity, whereas with CH_3SO_3H and iodine, unexpectedly, they increased clearly (an order of magnitude) in less polar solvents. The latter unusual trend comes from the fact that the monomer was consumed at appreciable rates (see Figure 5a) even when ΔOD_{380} was very small.

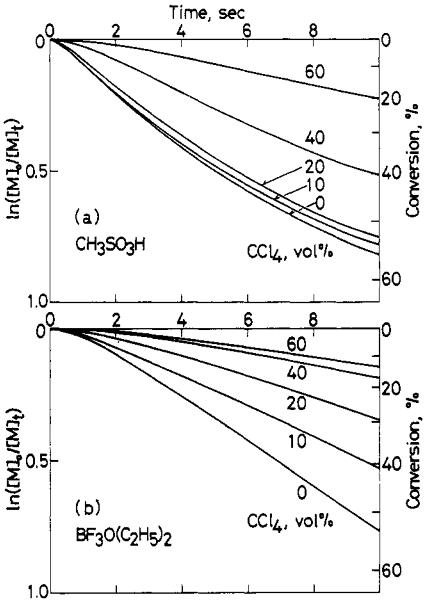

Figure 5. First-order plots for monomer consumption in $(CH_2Cl)_2$ /CCl_4 mixtures at 30 °C: $[M]_0 = 5.0$ mM; $[C]_0$ (CH_3SO_3H) 5.0 mM, ($BF_3 \cdot O(C_2H_5)_2$) 0.50 mM.

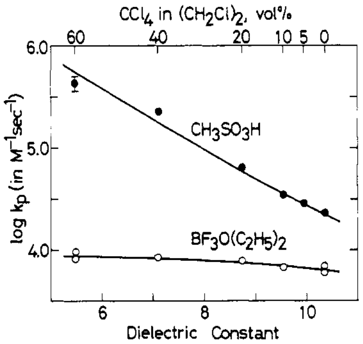

Figure 6. Dependence of propagation rate constant (k_p) on solvent dielectric constant. Data from Table I.

Table I
Solvent Effect on Propagation Rate Constants (k_p)[a] in *p*-Methoxystyrene Polymerization at 30 °C ($[M]_0 = 5.0 \times 10^{-3}$ M)[b]

Solvent, v/v $(CH_2Cl)_2$/ CCl_4	Dielectric Constant[c]	$k_p \times 10^{-4}$, $M^{-1} s^{-1}$ CH_3SO_3H	I_2	$BF_3 \cdot O(C_2H_5)_2$	$SnCl_4$
100/ 0	10.36	2.3[d]	0.47[d]	0.60[d]	1.2[d]
			0.48[d]	0.69	
95/ 5	9.95	2.9	0.56		
90/10	9.55	3.5	0.64	0.68	1.4
					1.4
80/20	8.74	6.4		0.78	1.3
60/40	7.11	23		0.85	
40/60	5.49	36–50[e]		0.83	
				0.97	

[a] k_p as defined by eq 1. [b] Initiator concentration (10^{-3} M): CH_3SO_3H, 5.0; I_2, 5.0; $BF_3 \cdot O(C_2H_5)_2$, 0.50; $SnCl_4$, 0.030. [c] Volume average calculated from the values for $(CH_2Cl)_2$ (10.36) and CCl_4 (2.238).[4] [d] Taken from ref 1. [e] Scattering is due to the very small absorbance at 380 nm in this solvent.

Thus, clear difference was found between the polymerizations by the two classes of initiators, CH_3SO_3H and $BF_3 \cdot O(C_2H_5)_2$. In the $BF_3 \cdot O(C_2H_5)_2$-initiated polymerization, an appreciable [P*] was observed even in nonpolar solvents and the k_p values hardly depended on solvent polarity. In the

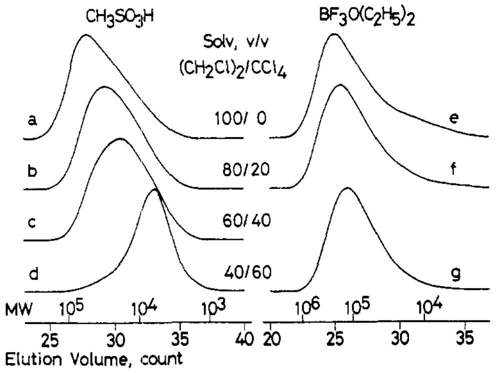

Figure 7. Solvent effect on the molecular weight distribution of poly(*p*-methoxystyrene) obtained in preparative polymerizations at 30 °C: $[M]_0 = 0.10$ M; $[C]_0$ (CH_3SO_3H) 2.0 mM, ($BF_3{\cdot}O(C_2H_5)_2$) 0.30 mM; molecular weight based on a polystyrene calibration.

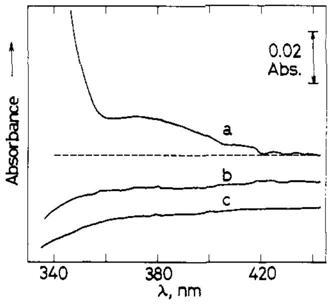

Figure 8. Absorption spectra of the polymerization solutions under preparative conditions at room temperature: $[M]_0 = 0.10$ M. Initiator ($[C]_0$) and solvent ($(CH_2Cl)_2/CCl_4$, v/v): (a) $BF_3{\cdot}O(C_2H_5)_2$ (0.30 mM), 40/60; (b) CH_3SO_3H (2.0 mM), 40/60; (c) CH_3SO_3H (2.0 mM), 5/95. Conversion: (a) 86%, (b) 90%, (c) 45%. Respective spectra are shifted vertically for easy comparison.

CH_3SO_3H-initiated polymerization, on the other hand, $[P^*]$ decreased nearly to zero in nonpolar solvents, while the k_p values steadily increased. These results indicate that the nature of the propagating species formed by CH_3SO_3H is much different in these nonpolar solvents from that in polar $(CH_2Cl)_2$.

One reasonable explanation for the steep increase of k_p values in the CH_3SO_3H-initiated polymerization in $(CH_2Cl)_2/CCl_4$ mixtures may be that the concentration of the propagating species is *underestimated* when determined from the absorbance at 380 nm. This implies that in nonpolar solvents another propagating species that has no absorption at 380 nm is present and can contribute to monomer consumption to a considerable extent. Thus, the monomer was polymerized at an appreciable rate even when ΔOD_{380} was very small. The involvement of this "invisible" (spectroscopically inactive) species, suggesting the multiplicity of the propagating species, was then examined in polymerizations under preparative conditions, because the stopped-flow experiments had to be done at a much lower $[M]_0$ (5.0 mM) than those in normal polymerizations.

Molecular Weight Distribution (MWD) of Polymers. With CH_3SO_3H and $BF_3{\cdot}O(C_2H_5)_2$ initiators, polymerizations at a higher $[M]_0$ (0.10 M) were carried out in $(CH_2Cl)_2/CCl_4$ mixtures, and the MWD of polymers produced was measured (Figure 7). Since all reaction conditions except for $[M]_0$ were the same as in the stopped-flow measurements, comparison should be possible between results of these preparative and spectroscopic experiments.

The MWD of polymers formed by CH_3SO_3H changed systematically with solvent polarity: a single high molecular weight peak in $(CH_2Cl)_2$ (Figure 7a) became broader and shifted to the low molecular weight side on addition of nonpolar CCl_4 (Figures 7b and 7c), and finally a new low molecular weight peak appeared in a highly nonpolar solvent (Figure 7d). The molecular weights of these high and low polymers were respectively (3–5) × 10^4 and ca. 6 × 10^3 (polystyrene calibration). The trend in MWD, coupled with those in the $[P^*]_{max}$ and k_p values shown above, indicates great changes in the nature of the propagating species in nonpolar solvents. Especially the appearance of the new peak strongly suggests involvement of another propagating species that was not present in polar $(CH_2Cl)_2$ solvent.

On the contrary, the $BF_3{\cdot}O(C_2H_5)_2$-initiated polymerization always yielded high molecular weight polymers with a unimodal MWD (Figure 7e–g). Their molecular weight ((1–2) × 10^5) changed little with solvent polarity. These correspond to the small solvent effect on k_p values described in the preceding section. Therefore, the propagating species derived from $BF_3{\cdot}O(C_2H_5)_2$ must have a similar reactivity in both polar and nonpolar solvents, although its dissociation state should vary with solvent polarity.

Multiplicity of the Propagating Species. The existence of the "invisible" species was further supported by absorption spectra of polymerization solutions under preparative conditions ($[M]_0 = 0.10$ M). Figure 8 shows their typical examples for CH_3SO_3H and $BF_3{\cdot}O(C_2H_5)_2$ initiators. The spectra of the CH_3SO_3H systems in nonpolar solvents (Figures 8b and 8c) exhibited no appreciable peak at 380 nm, while the monomer rapidly polymerized up to 90% conversion within 2–3 min. The products exclusively consisted of low molecular weight (ca. 10^4) polymers (cf. Figure 7d). It should be added here that the spectra were measured on really polymerizing solutions (i.e., taken at conversions less than 100%) and not on postpolymerization solutions. Therefore, these results demonstrate clearly the existence of the "invisible" propagating species in nonpolar solvents. The solvent effect on the MWD of polymers (Figure 7a–d) shows that this species produces the low molecular weight polymers and becomes more predominant in less polar media.

A contrast result was obtained for the $BF_3{\cdot}O(C_2H_5)_2$-initiated polymerization, in which a spectrum measured in a highly nonpolar solvent ($(CH_2Cl)_2/CCl_4$ = 40/60 v/v) still had an absorption at 380 nm (Figure 8a).[5] The MWD of polymers formed in this solvent consisted of only a high molecular weight peak as Figure 7g. Thus, the propagating species with the 380-nm absorption, which was also detected by stopped-flow spectroscopy, must form the high molecular weight polymers. It is predominant in the $BF_3{\cdot}O(C_2H_5)_2$ systems throughout or in the CH_3SO_3H systems in polar solvents.

The present work has thus presented evidence for the multiplicity of the propagating species, i.e., the existence of "invisible" and "visible" species:

invisible species	visible species (λ_{max} 380 nm)
↓	↓
low mol wt polymer	high mol wt polymer

The contribution of the "invisible" species was considerable in the CH_3SO_3H-initiated polymerization in nonpolar solvents, resulting in the observed increase of the k_p values determined from the 380-nm absorption. $BF_3{\cdot}O(C_2H_5)_2$ appears to always generate only the "visible" species irrespective of solvent polarity.

We could not observe any biomodal MWD of polymers[6] in the polymerization by CH_3SO_3H, although the above multiplicity of the propagating species suggests the possibility of a dual propagation mechanism. The absence of the bimodal MWD indicates that an interconversion, if present, between different propagating species is too fast to allow their independent propagation. This may result from a high stability of the propagating species derived from *p*-methoxystyrene and the relatively high reaction temperature (30 °C) employed here.

Interesting is a recent stopped-flow study[8,9] on the styrene polymerization by perchloric acid, in which an increase of k_p values was observed on addition of a perchlorate salt in methylene chloride. Decreasing solvent polarity in our work and the salt addition in the polar solvent in that study may have induced similar suppression of the ionic dissociation of the propagating species to give the "invisible" species. The nature of this species cannot be unambiguously described at present, although Pepper et al.[8,9] proposed covalent esters. However, since it has no absorption in the UV–visible region from 320 to 450 nm, it should be quite different in nature from free ionic carbocations.

Acknowledgment. Financial support from the Ministry of Education, Japanese Government is gratefully acknowledged.

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Kinetics of Styrene Addition in Benzene Solution to Living Lithium Polymers Terminated by 1,1-Diphenylethylene Units. The Effect of Mixed Dimerization of Monomeric Polymers

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ABSTRACT: The kinetics of addition of styrene to living polymers terminated by $-CH_2C(Ph)_2^-,Li^+$ was investigated in benzene. Under these conditions the reaction involves monomeric species; however, almost all the polymers exist in dimeric form. In our system the homodimers of lithium polystyryl and $Li-C(Ph)_2^-$ coexist in equilibrium with mixed dimers. The value of the association constant K_{12} characterizing the mixed dimerization is shown to be equal to $(K_1\cdot K_2)^{1/2}$, where $K_1/2$ and $K_2/2$ are the association constants of the respective homodimers. This relation is responsible for the first-order character of the addition, i.e., $-\{d \ln [\sim\sim C(Ph)_2^-,Li^+]/dt\}/[\text{styrene}] = k_{21}/K_2^{1/2}\cdot C_0^{1/2}$, where k_{21} is the bimolecular rate constant of addition of styrene to the monomeric $\sim\sim C(Ph)_2^-,Li^+$ and C_0 is the *total* concentration of *all* the living polymers, i.e., C_0 = [lithium polystyryl] + $[\sim\sim CH_2C(Ph)_2^-,Li^+]$. The importance of mixed dimers in other living systems involving Li salts in benzene is discussed.

On addition of an excess of 1,1-diphenylethylene, D, to lithium polystyryl in benzene, $\sim\sim S^-,Li^+$, a pseudo-first order reaction ensues,[1] its rate being monitored by the decay of $\sim\sim S^-,Li^+$ absorbance or by the appearance of absorption of $\sim\sim CH_2\cdot C(Ph)_2^-,Li^+$ pairs. Since D does not homopolymerize the reaction arising from

$$\sim\sim S^-,Li^+ + D \xrightarrow{k_{12}} \sim\sim CH(Ph)\cdot CH_2\cdot C(Ph)_2^-,Li^+ = \sim\sim D^-,Li^+$$

does not proceed further. The kinetics is peculiar in that the normalized pseudo-first-order constant, $k_u = -\{d \ln [\text{total } \sim\sim S^-,Li^+]/dt\}/[D]$, has been found to depend on the *initial* concentration of $\sim\sim S^-,Li^+$, namely $k_u \sim 1/[\text{total } \sim\sim S^-,Li^+]_0^{1/2}$. In other words, the rate R_t determined at constant concentration of D and measured at a time when the *total* concentration of lithium polystyryl has a fixed value depends also on the initial $[\text{total } \sim\sim S^-,Li^+]_0$, viz., R_t increases proportionally to $[\text{total } \sim\sim S^-,Li^+]_0^{1/2}$.

This peculiarity was accounted for by the following mechanism.[1] Lithium polystyryl is present in benzene in a dimeric, unreactive form which remains in equilibrium with the reactive monomeric species,[2]

$$(\sim\sim S^-,Li^+)_2 \overset{2/K_1}{\rightleftarrows} 2 \sim\sim S^-,Li^+$$

The observed addition of D involves this monomeric form, but as $\sim\sim D^-,Li^+$ is formed additional equilibria become established. It has been assumed that $\sim\sim D^-,Li^+$ homodimerizes as well as codimerizes with $\sim\sim S^-,Li^+$, i.e.,

$$(\sim\sim D^-,Li^+)_2 \overset{2/K_2}{\rightleftarrows} 2 \sim\sim D^-,Li^+$$

and

$$(\sim\sim D^-,Li^+,\sim\sim S^-,Li^+) \overset{1/K_{12}}{\rightleftarrows} \sim\sim D^-,Li^+ + \sim\sim S^-,Li^+$$

It was deduced[1] that

$$k_u = -\{d \ln [\text{total } \sim\sim S^-,Li^+]/dt\}/[D] = k_{12}/K_1^{1/2}C_0^{1/2}$$

where $C_0 = [\text{total } \sim\sim S^-,Li^+]_t + [\text{total } \sim\sim D^-,Li^+]_t = [\text{total } \sim\sim S^-,Li^+]_0$, provided that $K_{12} = (K_1\cdot K_2)^{1/2}$ and that the

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