Studies of Ion Pair Solvation: Absolute Rate Constants of Propagation of the Tetraglyme-co-ordinated Living Sodium Polystyrene

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Summary Studies of anionic polymerization of styrene in tetrahydropyran in the presence of tetraglyme led to the absolute value of the equilibrium constant K_G, $\text{—S}^-,\text{Na}^+ + \text{glyme} \rightleftarrows \text{—S}^-, \text{Na}^+ \text{(glyme)}$, and to the absolute value of the propagation constant of the "glymated" species

$$\text{—S}^-,\text{Na}^+\text{ (glyme)} + \text{S} \rightarrow \text{—S}^-\text{Na}^+\text{ (glyme)},\ k_G.$$

THE addition of tri- or tetra-glyme (G) to a solution of living sodium polystyrene ($\text{—S}^-,\text{Na}^+$) in tetrahydropyran (THP) has a profound effect upon the rate of propagation.[1] In the absence of glyme the polymerization is propagated by two species: the rapidly growing polystyryl carbanions, (—S^-), and the slowly growing ion pairs, ($\text{—S}^-,\text{Na}^+$), the latter forming the bulk of the growing ends. Thus,

$$\text{—S}^- + \text{S} \rightarrow \text{—S}^-, \qquad k_-, \tag{1}$$

$$\text{—S}^-,\text{Na}^+ + \text{S} \rightarrow \text{—S}^-,\text{Na}^+, \qquad k_\pm, \tag{2}$$

and

$$\text{—S}^-,\text{Na}^+ \rightleftarrows \text{—S}^- + \text{Na}^+, \qquad K_{\text{Diss}} \tag{3}$$

Two additional species are formed in the presence of tetraglyme (G), *viz.*,

$$—S^-,Na^+ + G \rightleftarrows —S^-,G,Na^+, \quad K_G, \tag{4}$$

yields the ion pairs co-ordinated with the glyme, and

$$Na^+ + G \rightleftarrows Na^+,G, \quad K_{Na}, \tag{5}$$

produces sodium ions complexed with the glyme. The $—S^-,G,Na^+$ ion pairs are more reactive than the tight $—S^-,Na^+$ pairs, their propagation constant being denoted by k_G. The acceleration of styrene polymerization resulting from the addition of glyme is caused, therefore by: (a) the conversion of the relatively unreactive $—S^-,Na^+$ ion pairs into much more reactive $—S^-,G,Na^+$ pairs; (b) the increase in the proportion of the highly reactive $—S^-$ free ions due to the conversion of Na^+ into Na^+,G. The magnitude of the effect is shown in Figure 2 of ref. 1, *e.g.*, in the presence of $2{\cdot}8 \times 10^{-3}$ M-tetraglyme, the observed propagation constant increases from 150 M^{-1} sec.$^{-1}$ to 3500 M^{-1} sec^{-1}.

The previously reported work[1] permitted us to determine the product $k_G K_G$. In the course of the present work we evaluated the individual constants. This was achieved by studying the polymerization at concentrations of tetraglyme sufficiently high to cause an extensive conversion of $—S^-,Na^+$ into $—S^-,G,Na^+$. Furthermore, extension of these studies to lower temperatures led to the determination of ΔH_G and ΔS_G (pertaining to equilibrium 4) and E_G (pertaining to reaction 6),

$$—S^-,G,Na^+ + S \rightarrow —S^-,G,Na^+, \quad k_G. \tag{6}$$

At any concentration of tetraglyme the intercept, I(G), of the line giving the observed propagation constant, k_p, as a function of [living polymers]$^{-\frac{1}{2}}$, is equal to $(1-f)k_{\pm} + fk_G$, f being the fraction of living polymers present as $—S^-,G,Na^+$. The intercepts may also be obtained by determining k_p as a function of $[Na^+]^{-1}$, the concentration of Na^+ ions being varied by the addition of Na^+,BPh_4^-. The second method is preferred since the lines are then flatter and extrapolation more reliable (see Figure 2 of ref. 1).

The relation $f/(1-f) = K_G[G]$ coupled with the inequality $k_G \gg k_{\pm}$ leads to the equation

$$\frac{1}{I(G) - I(O)} = \frac{1}{k_G} + \frac{1}{k_G K_G} \cdot [G]^{-1},$$

where I(O) is the intercept of the line obtained in the absence of tetraglyme. A plot of $1/\{I(G) - I(O)\}$ against $[G]^{-1}$ is exemplified by Figure 1 and its slope and intercept give eventually k_G and K_G. Thus, the experiments performed at 25°, 0°, −20°, and −45° led to the data summarized in the Table. Moreover, at lower temperatures k_G could be determined directly from the asymptotes of the plots of I(G) against [G] as shown in Figures 2a and b. Figure 2c shows in more detail the results obtained at 25°. The

TABLE

Equilibrium constant K_G *for the reaction*

$—S^-,Na^+ + G \rightleftarrows —S^-,G,Na^+$; (4),

and the rate constant k_G *of the propagation*

$—S^-,G,Na^+ + S \rightarrow —S^-,G,Na^+$; (6),

Solvent THP, G = *Tetraglyme*

T	K_G, M^{-1}	k_G, M^{-1} sec.$^{-1}$
25°	90	3900
0°	210	3500
−20°	770	2600
−45°	2000	2100

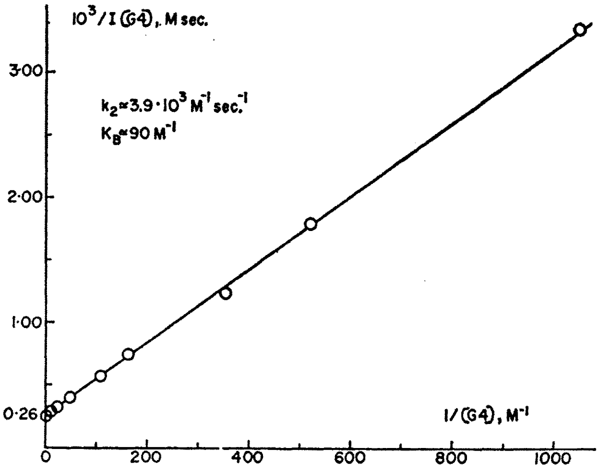

FIGURE 1

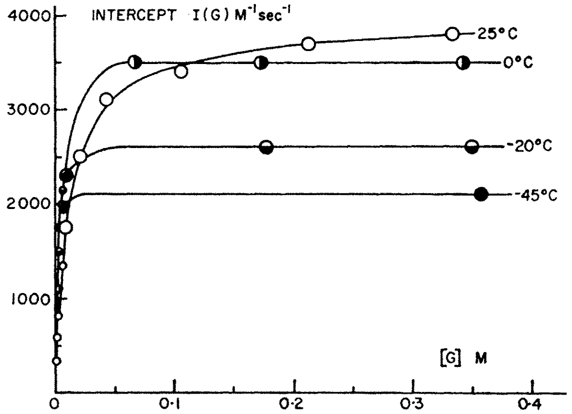

FIGURE 2a

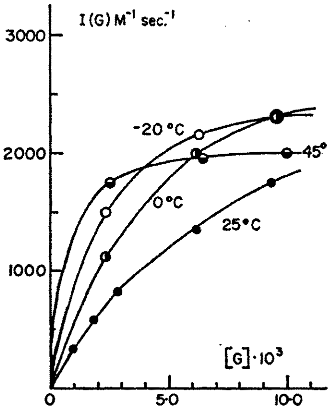

FIGURE 2b

initial slope and the asymtote permit us to evaluate k_G and K_G.

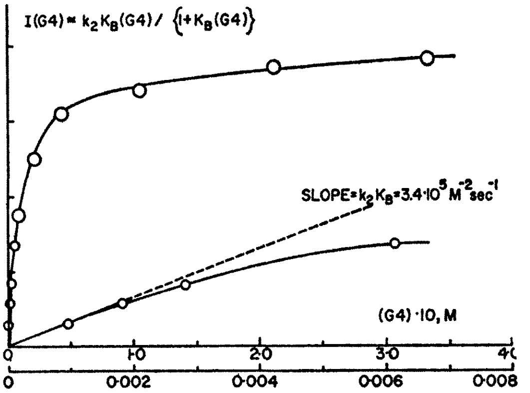

FIGURE 2c. *The lower scale refers to the lower curve.*

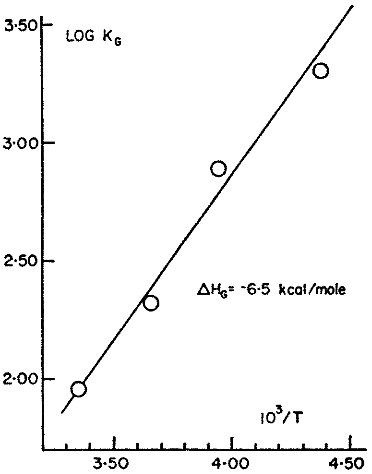

FIGURE 3

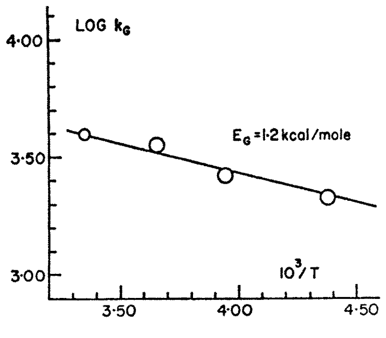

FIGURE 4

The van't Hoff plot (log K_G against $1/T$) and the Arrhenius plot (log k_G against $1/T$) are shown in Figures 3 and 4, respectively. From these $\Delta H_G = -6{\cdot}5$ kcal./mole, $\Delta S_G = -13$ e.u., and $E_G = 1{\cdot}2$ kcal./mole.

Closely similar values of ΔH_G and K_G were obtained in other systems. For example, for

$$\text{Biphenylide}^{\overset{-}{\cdot}},\text{Na}^+ + \text{G} \rightleftarrows \text{Biphenylide}^{\overset{-}{\cdot}},\text{G},\text{Na}^+$$

$\Delta H_G = -6{\cdot}0$ kcal./mole and K_G (at 21°) $= 75\ \text{M}^{-1}$ in THP,[2] and $-4{\cdot}6$ kcal./mole and $145\ \text{M}^{-1}$, respectively, in methyltetrahydrofuran;[2] for

$$\text{Fluorenyl}^-,\text{Na}^+ + \text{G} \rightleftarrows \text{Fluorenyl}^-,\text{G},\text{Na}^+ \text{ in THF}^3$$

$\Delta H_G = -7{\cdot}0$ kcal./mole and K_G (at 25°) $= 125\ \text{M}^{-1}$; for

$$\text{Naphthalenide}^{\overset{-}{\cdot}},\text{Na}^+ + \text{G} \rightleftarrows \text{Naphthalenide}^{\overset{-}{\cdot}},\text{G},\text{Na}^+ \text{ in THP}^4$$

K_G (at 25°) is about $200\ \text{M}^{-1}$. Apparently, the nature of anion and of solvent only slightly affects thermodynamics of tetraglyme co-ordination with the Na^+ ion of a tight ion pair.

The reactivity of $—\text{S}^-,\text{G},\text{Na}^+$, measured by the value of k_G, should be compared with those of "solvent separated" polystyryl sodium ion pairs. In tetrahydrofuran (THF) and in dimethoxyethane (DME) sodium ions become fully co-ordinated with solvent molecules[5] and their association with the anions yields the solvent separated pairs, provided the solvation shell is not squeezed out. The propagation constants of $—\text{S}^-(\text{THF})_n\text{Na}^+$ and $—\text{S}^-,(\text{DME})_m,\text{Na}^+$ ion pairs[6,7] are *ca.* $30{,}000\ \text{M}^{-1}$ sec.$^{-1}$ and $20{,}000\ \text{M}^{-1}$ sec.$^{-1}$, respectively, at 25°. Critical review of the relevant calculations convinces us that, in spite of some assumptions introduced in the derivation, these rate constants are substantially higher than K_G (*ca.* $4000\ \text{M}^{-1}$ sec.$^{-1}$). Hence, the "glymated" $—\text{S}^-,\text{G},\text{Na}^+$ ion pair, albeit loose, is appreciably less reactive than the loose living sodium polystyrene ion pairs solvated by THF or DME. Recent e.s.r. studies of "glymated" loose ion pairs[4] justify this result and show them to be tighter than the "solvent separated" pairs.

Finally, the unusually low value of E_G calls for comment. We tentatively suggest that $—\text{S}^-,\text{G},\text{Na}^+$ exists in two isomeric forms—a less reactive, which predominates at higher temperatures, and a more reactive which becomes abundant at lower temperatures. Evidence for such two isomers was first reported by Slates and Szwarc[2] for sodium biphenylide and more recently confirmation of this phenomenon was obtained from the e.s.r. studies[4] of glymated sodium naphthalenide ion pairs.

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