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Reactivities of Contact and Solvent-Separated Ion Pairs. Anionic Polymerization of Styrene in Dimethoxyethane

T. Shimomura, J. Smid, and M. Szwarc

Contribution from the Department of Chemistry, State University College of Forestry at Syracuse University, Syracuse, New York 13210.

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Abstract: Detailed studies of anionic polymerization of sodium and cesium salts of living polystyrene in dimethoxyethane (DME) led to the absolute rate constants of propagation for the $\sim\sim S^-,Na^+$ and $\sim\sim S^-,Cs^+$ ions pairs as well as for the free $\sim\sim S^-$ ions. These constants were determined over a temperature range +50 to −60°, providing therefore the necessary data for the calculation of the respective activation energies. The Arrhenius plot of the propagation constant of the $\sim\sim S^-,Na^+$ ion pair produced a curve with a maximum at 0°. This behavior was fully rationalized by assuming the presence of contact and solvent-separated $\sim\sim S^-,Na^+$ ion pairs. An analysis of the data led to the absolute rate constant of the solvent-separated ion pair. The thermodynamics of the dissociation and solvation processes involving ion pairs was fully elaborated.

Detailed studies of the kinetics of anionic polymerization revealed that its propagation involves ion pairs and free ions.[1-5] Living polymer systems offer many advantages in such investigations. Apart from an increase in the chain length, which does not affect its rate of growth, the initial and final states of the propagating species remain the same. For example

$$\sim\sim S^-,Na^+ + S \longrightarrow \sim\sim S^-,Na^+$$

i.e., the sodium salt of an n-meric living polystyrene ($\sim\sim S^-,Na^+$) is converted on the addition of a styrene molecule (S) into an $(n + 1)$-meric specie. Therefore, the progress of the reaction does not disturb the equilibrium established between the ion pairs and free ions or between the different types of ion pairs.

Investigation of living polystyrene propagation in tetrahydrofuran (THF) established the following facts.[2] (1) The bimolecular rate constant of growth of the free $\sim\sim S^-$ ion is 65,000 M^{-1} sec^{-1} at 25°. The activation energy of this propagation is about 5.9 kcal/mole, the respective A factor being 10^9 M^{-1} sec^{-1}. The rate constant decreases to about 1000 M^{-1} sec^{-1} at −60°, and further lowering of temperature changes only slightly its value. (2) The equilibrium constant of dissociation of $\sim\sim S^-,Na^+$ ion pairs into free ions is 1.5×10^{-7} M at 25°, the exothermicity of dissociation $-\Delta H = 9$ kcal/mole, its value decreasing to about 5 or 6 kcal/mole at −60°. This indicates that the $\sim\sim S^-,Na^+$ ion pair is virtually of a contact type in THF, although the proportion of the solvent-separated species increases considerably at the lowest temperatures. In contradistinction, the dissociation constant of the $\sim\sim S^-,Cs^+$ ion pair is much lower, about 5×10^{-9} M at 25°, and $-\Delta H = 1.8$ kcal/mole only. Apparently, the contact $\sim\sim S^-,Cs^+$ ion pair dissociates in THF into Cs^+ ion which is *not* coordinated with THF molecules, whereas the free Na^+ ion acquires a coordination shell. These conclusions are supported by studies of mobilities of sodium and cesium ions in THF.[6] (3) The rate constant

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(1) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

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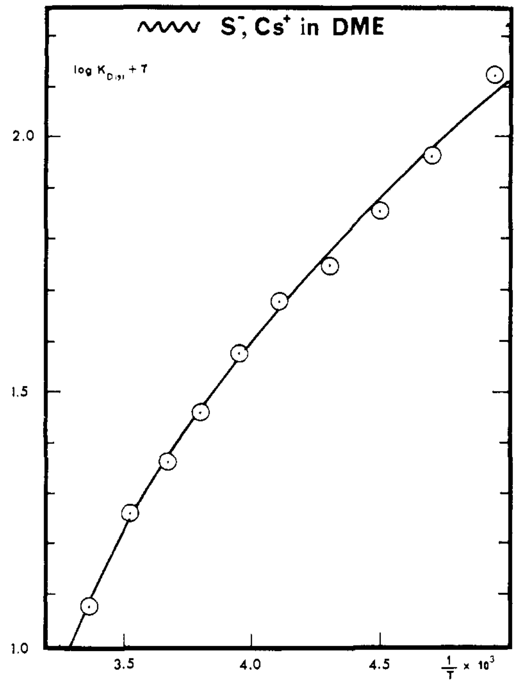

Figure 1. Plot of log K_{Diss} of $\sim\sim$S$^-$,Cs$^+$ ion pair in DME *vs.* $1/T$.

of the cesium ion-pair propagation in THF is about 21 M^{-1} sec^{-1} at 25°, the activation energy and the *A* factor being 5.7 kcal/mole and $\sim$2 × 10^5 M^{-1} sec^{-1}, respectively. The propagation rate constant of $\sim\sim$S$^-$, Na$^+$ is much higher, about 80–90 M^{-1} sec^{-1}, at 25°. Its value *increases* with decreasing temperature, being 280 M^{-1} sec^{-1} at $-80°$. The intriguing "negative activation energy," which amounts to about -1.5 kcal/mole, indicates that the propagation is due to solvated (coordinated) ion pairs, the fraction of which increases at lower temperatures. Collating all the evidence, it was possible to deduce that the propagation constant of the solvent-separated sodium ion pair in THF is about 20,000–30,000 M^{-1} sec^{-1} at 25°, and the heat of conversion of the contact pair into the solvent-separated pair amounts to about -7 kcal/mole.

It is known[7,8] that dimethoxyethane (DME) is a much more powerful coordinating agent than THF. In fact, conductance studies of tetraphenylboride salts in DME demonstrated[6] that even the free Cs$^+$ ion becomes coordinated with DME, although its coordination with THF is negligible. It was decided, therefore, to investigate the polymerization of living polystyrene in this medium, in anticipation that the proportion of solvent-separated ion pairs should be substantially higher than that observed in THF. The results reported in this paper fully confirmed this expectation.

Experimental Section

Dimethoxyethane (DME) was refluxed over sodium–potassium alloy until the reaction with alkali metal had ceased. Thereafter, the solvent was fractionated on a high-vacuum line; the middle fraction was collected and again allowed to react with Na-K alloy to which some benzophenone was added. The solvent was redistilled onto a dry living polymer, left in contact with it for a few hours and distilled again into the apparatus used in kinetic studies. The desired experiment was then performed without any delay. The living polymer dissolved in a not too carefully purified DME undergoes a relatively rapid reaction which converts the $\sim\sim$CH$_2$CH(Ph)$^-$ carbanion into more stable species. This change is reflected by the appearance of new peaks in the spectrum of the living polymer solution.

The solution of the cesium salt of living polystyrene in the purified DME is sufficiently stable to permit determination of its conductance. Unfortunately, the solution of the sodium salt is much less stable, and a substantial fraction of the carbanions is destroyed in about an hour. This prevented us from determining the conductance of the sodium salt in DME. Nevertheless, the kinetic studies involving the sodium salt were possible if the following procedure was adopted. The sodium salt was prepared in tetrahydrofuran (THF). The solution was then introduced into one of the compartments of the apparatus used in kinetic studies, details of which were described elsewhere,[2] and the solvent removed under high vacuum. Purified DME and monomer solution were stored in other ampoules. After evacuation the unit was sealed and brought to the desired temperature. The living polymer then was dissolved rapidly in DME and mixed with the monomer, and the progress of polymerization was followed spectrophotometrically by recording the decrease of optical density at 291.5 mμ (a characteristic peak of styrene). A detailed description of the kinetic runs is given in ref 2. The polymerization was completed in less than a minute and the living polymer remained in contact with DME for not more than 10 min prior to the onset of the reaction.

Further details of the procedure used in kinetic studies of polymerization of the sodium and cesium salts of living polystyrene, as well as the details of the conductance studies, are given in ref 1, 2, and 6. Living polystyrenes were always prepared in THF. The solvent was then evaporated under vacuum and the purified DME distilled in. The living polystyrene possessing the Cs$^+$ counterion was endowed with only one growing end, its preparation being described in ref 1 and 2.

Results and Discussion

Conductance Studies of Cesium Salt of Living Polystyrene. The conductance data for polystyrylcesium in DME are reported in Table I. Fuoss plots of F/Λ *vs.* $c\Lambda f^2/F$ were obtained for ten temperatures at intervals of 10°. The Λ_0 values were calculated by adding λ_0(Cs$^+$) determined in DME[6] to λ_0($\sim\sim$S$^-$) calculated on the basis of Walden rule from the data obtained in THF. The application of Walden rule does not introduce any large error because λ_0($\sim\sim$S$^-$) is only a small fraction of λ_0(Cs$^+$), and the specific solvation of the anion is insignificant in both solvents. The dissociation constants are listed in Table I, and plot of log $K_{\mathrm{Diss,Cs^+}}$ *vs.* $1/T$ is shown in Figure 1. At room temperature the dissociation constant of $\sim\sim$S$^-$,Cs$^+$ in DME is comparable to that of $\sim\sim$S$^-$,Na$^+$ in THF and about 20 times larger than that of the cesium salt in THF. These results are consistent with the data obtained for CsBPh$_4$ in these solvents.[6] The exothermicity of dissociation in DME is about 4 kcal/mole, substantially larger than in THF ($-\Delta H$ = 1.8 kcal/mole), confirming our previous observations that the free cesium is coordinated with DME molecules.[6] Neither the ion pair nor the free cesium ion appears to be coordinated with the solvent in THF. The slope of the log $K_{\mathrm{Diss,Cs^+}}$ *vs.* $1/T$ decreases gradually with temperature as predicted from the Denison–Ramsey equation relating the $-\Delta H$ of dissociation with the temperature dependence of the dielectric constant. However, its value is still about -2.5 kcal/mole at $-70°$, indicating that if any solvent-separated ion pairs are formed their fraction is rather small, even at $-70°$. The exothermicity of formation of the solvent-separated ion pair from the contact ion pair is probably relatively low, a conclusion which, as we shall see, is confirmed by the kinetic data.

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(6) C. Carvajal, K. J. Tölle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **87**, 5548 (1965).

(7) F. Cafasso and B. R. Sundheim, *J. Chem. Phys.*, **31**, 809 (1963).

(8) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307 (1966).

Table I. Dissociation Constant of $\sim\!\sim S^-,Cs^+$ (One Living End) in DME

Temp, °C	Λ_0,[a] cm^2 ohm^{-1} equiv^{-1}	Slope of Fuoss line, $K_{Diss}{}^{-1}\Lambda_0{}^{-2}$ $\times 10^{-4}$	$K_{Diss} \times 10^7$ [b] M
25	67.9	0.182	1.2 (0.85)
10	58.1	0.163	1.8 (1.6)
0	51.1	0.167	2.3
−10	44.4	0.178	2.8
−20	38.1	0.184	3.8
−30	31.9	0.210	4.7
−40	26.4	0.258	5.6
−50	21.4	0.308	7.1
−60	16.5	0.400	9.2
−70	12.1	0.513	13.3

[a] $\Lambda_0 = \lambda_0{}^+ + \lambda_0{}^-$, $\lambda_0{}^+$ from ref 3, $\lambda_0{}^-$ calculated, by using Walden rule, from the $\lambda_0{}^-$ values for $\sim\!\sim S^-$ in THF given in ref 1. [b] The values given in parentheses are obtained from the kinetic runs in the presence and absence of $Cs^+,BPh_4{}^-$ (see Table IV).

Table II. Polymerization of $\sim\!\sim S^-,Cs^+$ (One Living End) in DME in the Absence of Salt

Temp, °C	$[\sim\!\sim S^-,Cs^+]$ $\times 10^4$ M	$[S]_0$ $\times 10^3$ M	$1/[LE]^{-1/2}$ [a]	k_p, M^{-1} sec^{-1}
25	0.39	2.41	161	2300
	0.485	2.70	144	2110
	0.54	2.53	136	1980
	0.89	2.05	106	1510
	1.00	2.38	100	1440
	2.50	2.00	63	970
	2.90	15.4	59	825
	6.6	12.35	39	565
	8.6	13.5	34	525
	8.9	6.9	34	490
0	1.25	3.0	89	775
	1.3	2.26	87	810
	1.4	2.56	84	730
	1.75	2.38	75	635
	1.75	1.92	75	640
	1.8	1.91	74	655
	2.8	2.03	59	530
	4.25	13.8	48	415
	4.5	13.2	47	445
	7.4	13.0	37	340
	10.6	12.2	31	280
−30	0.83	2.03	110 (121)	520
	1.3	1.92	88 (98)	435
	1.6	2.23	80 (90)	410
	2.0	2.22	70 (79)	355
	2.15	2.00	69 (78)	340
	2.4	2.44	64 (72)	335
	2.7	2.23	61 (69)	300
	4.4	11.1	47 (53)	245
	6.7	13.2	39 (45)	200
	14.0	6.65	27 (38)	140
−60	1.0	1.35	100 (112)	120
	1.3	1.95	88 (100)	112
	1.5	1.85	81 (92)	102
	1.6	1.97	78 (89)	95
	2.3	3.10	66 (75)	76
	2.95	0.67	58 (67)	69
	3.0	1.43	58 (67)	70.5
	3.3	10.6	55 (63)	70
	4.5	13.6	47 (55)	62
	6.2	14.3	40 (47)	58
	9.7	10.0	32 (38)	46

[a] The corrected values in parentheses were obtained by introducing the activity coefficients.

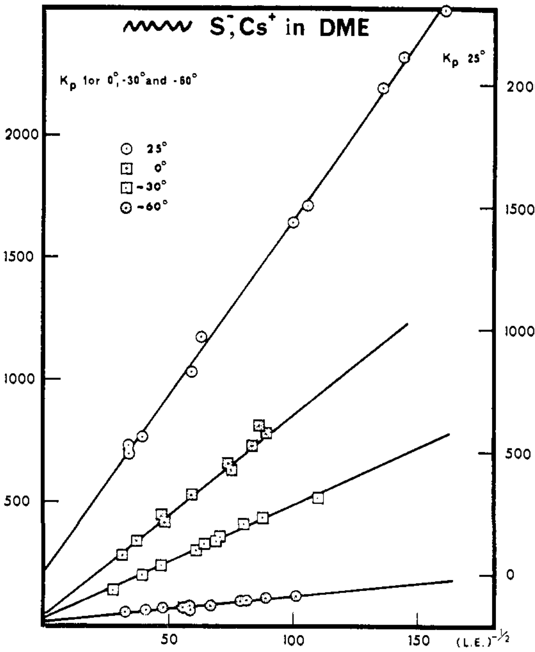

Figure 2. Plot of k_{ap} of propagation of $\sim\!\sim S^-,Cs^+$ ion pair in DME *vs.* $[\sim\!\sim S^-,Cs^+]^{-1/2}$. The intercepts give the propagation rate constant of $\sim\!\sim S^-,Cs^+$ ion pair. The slopes are equal to $(k_- - k_{\pm,Cs^+})\cdot(K_{Diss,S^-,Cs^+})^{1/2}$.

Polymerization of Polystyrylcesium in DME. The homopolymerization of polystyrylcesium in DME was measured over a wide range of living ends concentration at 25, 0, −30, and −60°. Plots of $[LE]^{-1} \log \{(OD_{291.5})_0 - (OD_{291.5})_\infty\}/\{(OD_{291.5})_t - (OD_{291.5})_\infty\}$ *vs.* time were linear, the slopes giving the respective apparent propagation rate constants k_p listed in Table II. Since the fraction of free ions is small, the observed rate constant k_p is given by

$$k_p = k_\pm + (k_- - k_\pm)K_{Diss}{}^{1/2}/[LE]^{1/2}$$

where [LE] is the total concentration of living polymers, and $k_\pm$ and k_- are the respective propagation constants of the ion pair and the free ion. Plots of k_p *vs.* $(\sqrt{[LE]})^{-1}$ yielded straight lines as shown in Figure 2. At two temperatures, *i.e.*, 0 and 25°, additional experiments were performed in the presence of a strongly dissociated cesium salt, *viz.*, $Cs^+BPh_4{}^-$. The relevant data are shown in Table III. In this case plots of k_p *vs.* $[Cs^+]^{-1}$ are linear (see ref 1 and 2). The concentration of cesium cations could be calculated from the known dissociation constants of $CsBPh_4$ in DME.[6]

The intercepts and slopes of the lines shown in Figure 2 are listed in Table IV. The former give the propagation rate constants, $k_{\pm,Cs^+}$ of the $\sim\!\sim S^-,Cs^+$ ion pairs, whereas the latter are equal to the product $(k_- - k_\pm)K_{Diss,\sim\sim S^-,Cs^+}{}^{1/2}$. The plots of k_p *vs.* $1/[Cs^+]$, obtained from the data collected in Table III, are also linear and their intercepts and slopes are also listed in Table IV. The latter intercepts give again the respective $k_{\pm,\,Cs^+}$, the reliability being, however, higher because the relevant lines are less steep than those shown in Figure 2. The slopes are equal to $(k_- - k_\pm)\cdot K_{Diss,\sim\sim S^-,Cs^+}$. These slopes in conjunction with those obtained in the absence of salt lead to the propagation rate constants k_- of the free $\sim\!\sim S^-$ ion (Table V) and to the dissociation constants $K_{Diss,\sim\sim S^-,\,Cs^+}$ of the $\sim\!\sim S^-$, Cs^+

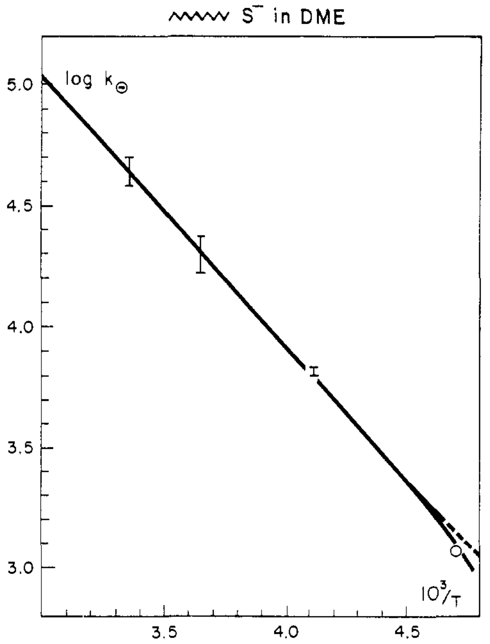

Figure 3. The propagation rate constant k_- of the $\sim\sim S^-$ free ion in DME. Plot of log k_- *vs.* $1/T$.

ion pair (see Table IV). No recourse to the conductance data is needed in these calculations.

Table III. Polymerization of $\sim\sim S^-,Cs^+$ (One Living End) in DME in the Presence of Excess of Cs^+,BPh_4^-

Temp, °C	$[\sim\sim S^-,Cs^+]$ × 10^4 *M*	$[Cs^+,BPh_4^-]$ × 10^4 *M*	$[Cs^+]^{-1}$ × 10^{-3} M^{-1} [a]	k_p(obsd), M^{-1} sec^{-1}
25	1.57	14.6	5.11 (7.10)	196
	1.60	15.7	5.05 (7.00)	191
	1.64	7.40	7.60 (10.2)	204
	3.00	7.20	7.70 (10.3)	203
	1.25	4.35	10.2 (13.2)	205
	1.44	3.85	10.9 (14.2)	219
	1.83	2.70	13.3 (17.0)	228
	1.89	2.20	16.2 (20.3)	238
0	1.68	10.85	4.70 (6.53)	77
	1.55	7.50	5.80 (7.96)	78
	0.93	4.53	7.70 (10.3)	88
	1.18	4.24	8.05 (10.7)	80
	1.80	3.02	9.90 (13.0)	88
	1.31	2.54	10.9 (14.2)	90
	1.39	1.80	13.5 (17.3)	101
	1.41	1.35	16.3 (20.3)	110
	1.00	1.35	16.3 (20.3)	103
	0.73	1.25	17.1 (21.4)	125
	1.04	1.22	17.4 (21.8)	115

[a] The corrected values (in parentheses) were obtained by introducing the activity coefficients. $[Cs^+]$ was calculated from the dissociation of Cs^+,BPh_4^-. The required dissociation constant was taken from C. Carvajal, *et al.*, *J. Am. Chem. Soc.*, **87**, 5548 (1965). Dissociation of $\sim\sim S^-,Cs^+$ contributes negligibly to the concentration of Cs^+ ions.

The conventional mass law is assumed; *i.e.*, the activity coefficients of the respective ions are taken as unity. In some of our experiments the concentrations of free ions are rather large and it seems that the activity coefficients should be introduced. The equilibrium constants derived from the conductance data need no corrections. They are obtained from experiments performed at very high dilution, and in addition the Fuoss treatment includes the activity coefficients. However, the concentrations of the ions calculated from the equation $K_{\text{Diss}} = [A^+][B^-]/[A^+,B^-]$ should be replaced by those obtained from the relation

$$K_{\text{Diss}} = [A^+][B^-]\gamma_\pm^2/[A^+,B^-]$$

Therefore, the "corrected" ratio $[\sim\sim S^-]/[\sim\sim S^-,A^+]$ is given by $(K_{\text{Diss}}^{1/2}/[\text{LE}]^{1/2}\gamma_\pm)$ in the absence of additional salt and by $(K_{\text{Diss}}/[A^+]\gamma_\pm)$ in the presence of tetraphenyl boride ($[A^+]$ denotes the "uncorrected" concentration of the cations). Hence, $1/[\text{LE}]^{1/2}\gamma_\pm$ should replace $1/[\text{LE}]^{1/2}$ in plots shown in Figure 2, and $1/[A^+]\gamma_\pm$ should replace $1/[A^+]$ in plots constructed from the data given in Table III. In the respective tables the "corrected" coordinates are given in parentheses.

The activity coefficients, $\gamma_\pm$, were calculated from the experimental $\gamma_\pm$'s reported for aqueous sodium chloride taking into account that the equivalent concentrations of ions in DME should be increased by the factor $(D_{H_2O}T)^{3/2}/(D_{\text{DME}}T)^{3/2}$ to be comparable with the aqueous data. The use of the equation involving ionic strength is not recommended because the deviations from Debye's law of dilute electrolyte solutions are too large. When the "corrected" coordinates were used the relevant plots were as linear as those derived from the "uncorrected" data.

Inspection of Tables IV, V, and VIII shows that the corrections have only a minor effect on the final results. In fact, judging from the dissociation constants given in Tables I and IV, the "uncorrected" values are more consistent with those derived from the conductance experiments than the "corrected" ones. Consequently, the averages of both are used in further calculations.

The propagation rate constants of $\sim\sim S^-$ ions are given in Table V. The various approaches led to slightly different results all of which are included in the plot of log k_- *vs.* $1/T$ shown in Figure 3. The most probable

Table IV. Polymerization of $\sim\sim S^-,Cs^+$ (One Living End) in DME[a]

Temp, °C	No Cs^+,BPh_4^- present: $k_\pm$, M^{-1} sec^{-1}	No Cs^+,BPh_4^- present: $(k_- - k_\pm)\cdot K_{\text{Diss}}^{1/2}$	Cs^+,BPh_4^- present: $k_\pm$, M^{-1} sec^{-1}	Cs^+,BPh_4^- present: $(k_- - k_\pm)\cdot K_{\text{Diss}}^{1/2}$
25	...	13.0	~150 (170)	0.0038 (0.0034)
0	~60 (41)	7.9	60 (57)	0.0032 (0.0027)
−30	30 (<10)	4.6 (4.3)		
−60	10 (<10)	1.1 (1.1)		

$K_{\text{Diss},\sim\sim S^-,Cs^+}$ (at 25°) = 0.85×10^{-7} *M* (0.2×10^{-7})
(at 0°) = 1.7×10^{-7} *M* (1.2×10^{-7})

[a] The values given in parentheses were obtained when introducing the activity coefficients.

Table V. Reactivity of the Free $\sim\sim S^-$ in DME[a]

Temp, °C	k_-, M^{-1} sec^{-1}: Set I	k_-, M^{-1} sec^{-1}: Set II
25	45,700 (50,000)	38,000 (38,000)
0	20,000 (23,000)	16,500 (16,500)
−30	...	6,700 (6,300)
−60	...	1,160 (1,160)

[a] Set I: values calculated by combining the kinetic data for $\sim\sim S^-,Cs^+$ in the presence and absence of salt. Set II: value calculated from kinetic data for $\sim\sim S^-,Cs^+$ in the absence of salt, combined with the conductance data for K_d. The values in brackets are obtained when the activity coefficients are introduced.

Table VI

Solvent	k_- (25°), M^{-1} sec^{-1}	E_-, kcal/mole	A_-, M^{-1} sec^{-1}	Ref
DME	~40,000	~5.0	~2×10^8	This work
THF	65,000	5.9	1×10^9	2
THP	59,000–72,000	...	...	To be published
2-MeTHF	27,000–30,000	...	...	To be published
THF-dioxane	~60,000	...	...	4a
THF-benzene	40,000–70,000	...	...	4b

Table VII. Polymerization of $\sim$S$^-$,Na$^+$ in DME

Temp, °C	[$\sim$S$^-$,Na$^+$] $\times 10^4$ M	[Na$^+$,BPh$_4^-$] $\times 10^4$ M	[Na$^+$]$^{-1}$ $\times 10^{-3}$ M^{-1} [a]	k_p(obsd), M^{-1} sec^{-1}
50	1.39	90.5	2.08 (3.16)	2880
	0.88	21.9	3.42 (4.96)	3060
	0.96	14.9	4.03 (5.68)	3000
	0.46	7.35	6.47 (8.9)	3070
	0.63	4.69	8.35 (11.1)	3220
25	1.24	121.5	1.29 (1.98)	3690
	0.81	40.6	2.26 (3.37)	3800
	0.71	37.2	2.35 (3.51)	3680
	0.95	21.2	3.19 (4.62)	3910
	1.27	15.8	3.65 (5.24)	3850
	0.57	11.6	4.43 (6.24)	3830
	0.88	10.2	4.75 (6.60)	3820
	0.58	4.76	7.38 (9.8)	4100
	1.10	5.75	6.60 (8.9)	4000
0	0.93	45.3	1.92 (2.91)	4390
	0.68	28.7	2.45 (3.60)	4450
	0.62	21.3	3.20 (4.64)	4450
	0.95	14.0	3.62 (5.17)	4500
	1.21	16.0	3.70 (5.29)	4540
	0.84	10.85	4.18 (5.89)	4700
	0.64	7.30	5.34 (7.28)	4800
−30	1.09	67.0	1.30 (2.00)	3040
	1.09	30.8	2.00 (3.03)	3380
	0.75	19.5	2.55 (3.75)	3450
	0.90	9.45	3.82 (5.46)	3750
	0.64	7.75	4.31 (6.07)	3820
	1.27	5.20	5.49 (7.63)	3970
	0.86	2.93	7.81 (10.4)	4500
−60	1.24	109.5	0.81 (1.25)	1110
	1.44	29.4	1.57 (2.38)	1340
	1.06	13.1	2.63 (3.87)	1420
	1.25	10.1	3.05 (4.42)	1390
	1.14	6.65	3.96 (5.58)	1690
	1.06	4.84	4.81 (6.68)	1580
	1.22	3.04	6.54 (8.8)	1820
	1.14	2.86	6.66 (8.9)	1770

[a] The corrected values obtained by introducing activity coefficients.

Table VIII. Reactivity and Dissociation Constants of $\sim$S$^-$,Na$^+$ in DME[a]

Temp, °C	$k_\pm$, M^{-1} sec^{-1}	$K_{\mathrm{Diss,Na^+}}(k_- - k_\pm)$	$K_{\mathrm{Diss}}{}^{b} \times 10^6$ M
50	2900 (2800)	0.04 (0.035)	0.5 (0.45)
25	3600 (3600)	0.054 (0.045)	1.4 (1.1)
0	4100 (4100)	0.125 (0.094)	7.8 (5.9)
−30	2900 (2800)	0.21 (0.16)	62 (46)
−60	1100 (?) (1000)	0.11 (0.10)	310[c] (220)[c]

[a] The values in parentheses were obtained on introducing the activity coefficient. [b] Calculated from k_- taken from the graph of log k_- *vs.* $1/T$. The value at 50° was obtained by extrapolation (Figure 3). [c] Based on the linearly extrapolated $k_- = 1450$ M^{-1} sec^{-1} (Figure 3).

values of k_- are read from the line. The respective activation energy is about 5 kcal/mole and the corresponding A factor about 2×10^8 M^{-1} sec^{-1}.

It is interesting to compare the behavior of free $\sim$S$^-$ ions in DME and in other ethereal solvents (Table VI). It seems that the free negative carbanion interacts only weakly with ethereal solvents and, hence, the nature of such an environment has only a negligible effect upon its reactivity. We shall see that the situation is drastically different for the ion-pair reactivities which are enormously affected by the solvent.

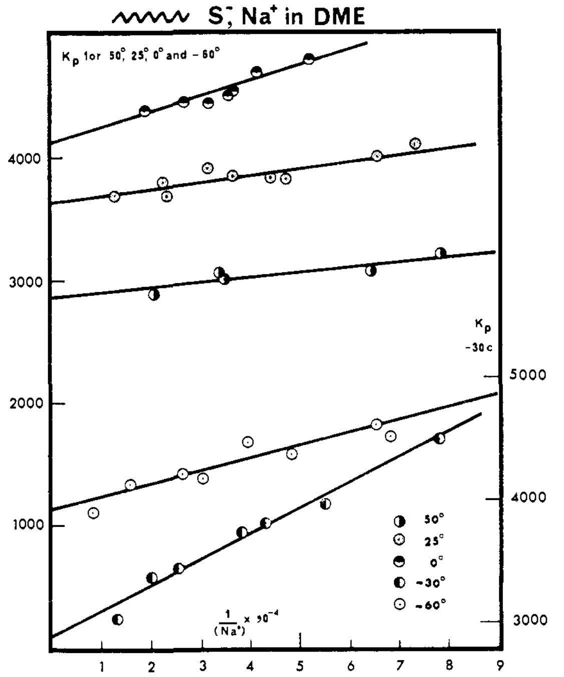

Figure 4. Plot of k_{ap} of propagation of $\sim$S$^-$,Na$^+$ ion pair in DME. The intercepts give the propagation constant of $\sim$S$^-$,Na$^+$ ion pair. The slopes are equal to $(k_- - k_{\pm,\mathrm{Na^+}})K_{\mathrm{Diss,S^-,Na^+}}$.

Polymerization of Polystyrenesodium in DME. Polymerization of living polystyrenesodium in DME is very rapid, and therefore it was necessary to investigate its kinetics in the presence of sodium tetraphenylboron in order to slow down the reaction. The pertinent results are listed in Table VII and presented graphically in Figure 4. Although this salt was in contact with DME for less than 10 min, destruction of the active ends was not negligible. The "killing" required introduction of appropriate corrections in the calculation of the observed rate constants, and this complicating factor is probably responsible for some degree of scatter of the experimental points (see Figure 4). The intercepts and slopes are listed in Table VIII. One may see again that introduction of activity coefficients had only a minor effect upon the final results.

The labile nature of DME solutions of $\sim$S$^-$,Na$^+$ prevented us from studying its conductance. Con-

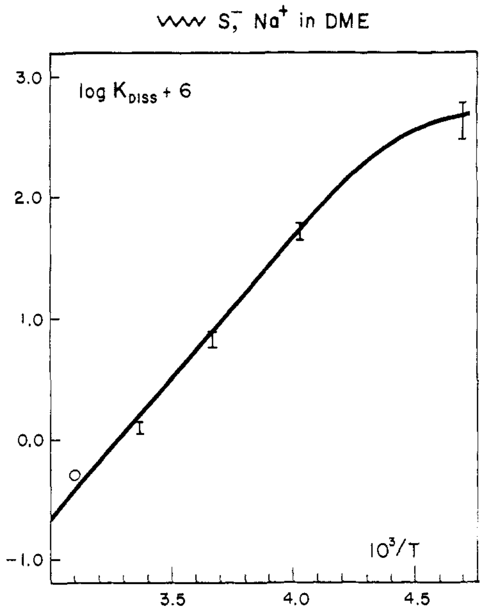

Figure 5. Plot of log K_{Diss} of ∼S$^-$,Na$^+$ ion pair in DME *vs.* $1/T$.

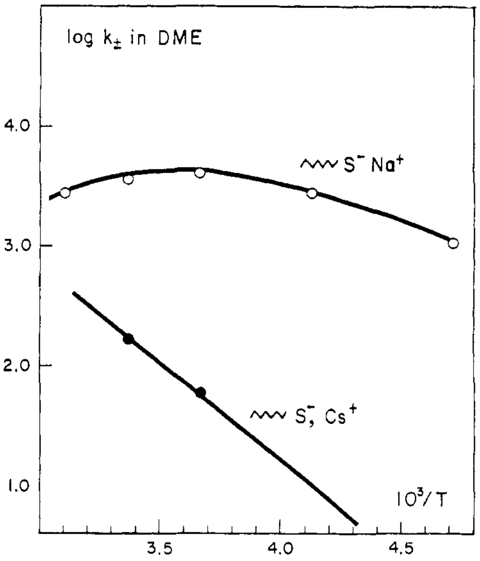

Figure 6. Propagation constants, $k_\pm$, of ∼S$^-$,Cs$^+$ and ∼S$^-$,Na$^+$ ion pairs in DME, plotted as log $k_\pm$ *vs.* $1/T$.

sequently, the relevant dissociation constants, $K_{\mathrm{Diss,Na^+}}$, were calculated from the slopes of the lines shown in Figure 4, which give $(k_- - k_\pm)K_{\mathrm{Diss,Na^+}}$, in conjunction with the values for k_- derived from the kinetic studies of ∼S$^-$,Cs$^+$. The results are listed in Table VIII and displayed graphically in Figure 5. The heat of dissociation is -11 kcal/mole at about 0° corresponding to $\Delta S = -63$ eu. The respective values for this salt in THF are $\Delta H = -9$ kcal/mole and $\Delta S = -60$ eu.

Propagation of Styrene Polymerization by Ion Pairs. The available data demonstrate that the reactivities of ion pairs are greatly affected by solvent. For example, at 25° the propagation rate constant, $k_{\pm,\mathrm{Cs^+}}$, of the ∼S$^-$,Cs$^+$ ion pair is about 20–25 M^{-1} sec^{-1} in dioxane,[9b] tetrahydrofuran,[1,2] and 2-methyltetrahydrofuran,[10] but about 150 M^{-1} sec^{-1} in dimethoxyethane. Even larger variations are observed for the ∼S$^-$,Na$^+$ ion pair. $k_{\pm,\mathrm{Na^+}}$ is 3-5 M^{-1} sec^{-1} in dioxane,[9] about 80 M^{-1} sec^{-1} in tetrahydrofuran,[1,2] and 3600 M^{-1} sec^{-1} in dimethoxyethane. These enormous changes suggest that two *different* ∼S$^-$,Na$^+$ ion pairs participate in the reaction: the unreactive contact pair and the highly reactive solvent-separated pair. Since the solvation process leading from the contact to the solvent-separated pair is exothermic, their proportion increases with decreasing temperature. Moreover, if the heat of solvation, $-\Delta H_s$, is greater than the activation energy, E_s, of the propagation by solvent-separated pairs, the observed "activation energy" may be negative, as indeed has been found for ∼S$^-$,Na$^+$ polymerization in tetrahydrofuran.[2]

The proposed treatment predicts that the curve produced by plotting log $k_\pm$ as a function of $1/T$ should have a maximum, and, as shown in Figure 6, this is indeed the case for the ∼S$^-$,Na$^+$ propagation in DME. The respective temperature, $T_{\max}$, is given by the condition $E_s + \Delta H_{\mathrm{solv}}/(1 + K_{\mathrm{solv}}) = 0$. In this equation E_s is the activation energy of propagation of solvent-separated ion pair, and K_{solv} and ΔH_{solv} are the equilibrium constant and the heat, respectively, of the solvation process converting the contact pair into the solvent-separated one. The contribution of the contact pairs to the reaction is believed to be negligible.

Let us accept now the following reasonable values: $E_s = 5$ kcal/mole (the same as for the free ion propagation) and $\Delta H_{\mathrm{solv}} = -7$ kcal/mole (the heat of dissociation of contact ∼S$^-$,Na$^+$ pairs into free ions has been found to be about 11 kcal/mole in DME). These values give $K_{\mathrm{solv}} \sim 0.4$ at $T_{\max} = \sim 0°$. Hence, about 29% of the ion pairs form the solvent-separated species at this temperature. Since at 0° $k_\pm = 4100\ M^{-1}$ sec^{-1}, the propagation constant of the solvent-separated ∼S$^-$,Na$^+$ pair is 14,000 M^{-1} sec^{-1}. The propagation constant of the free ∼S$^-$ ion is at this temperature $\sim$20,000 M^{-1} sec^{-1}; hence, the propagation constant of the solvent-separated pair appears to be one-third lower than that of the free ions. A similar conclusion was reached from previous studies of the tetrahydrofuran system.[2] Therefore, K_{solv} may be calculated at other temperatures from the respective $k_{\pm,\mathrm{Na^+}}$ if the rate constant of the separated ion pair is assumed to be given by $^2/_3k_-$. Such calculations lead to the values of 0.055, 0.13, 0.41, and 1.85 for $T = 50$, 25, 0, and $-30°$, respectively. A plot of log K_{solv} *vs.* $1/T$ is linear, and from it ΔH_{solv} is calculated to be -6.9 kcal/mole in agreement with our original assumption. The assumption that solvent-separated ∼S$^-$,Na$^+$ ion pairs are important propagating species in DME and THF is therefore justified, and our choice of ΔH_{solv} and $E_{\mathrm{solv,Na^+,S^-}}$ is upheld. Moreover, on the basis of the observed $\Delta H_{\mathrm{Diss,Na^+}}$, the heat of dissociation of contact and solvent-separated ∼S$^-$,Na$^+$ ion pairs is -11 and -4 kcal/mole, respectively.

Is the higher reactivity of ∼S$^-$,Cs$^+$ in DME due to the contribution of a small fraction of solvent-separated ion pairs? This is an attractive explanation, but we do not feel that it satisfactorily solves the whole problem. The entropies of dissociation of ∼S$^-$,Cs$^+$ in THF and DME are -44 and -46 eu, respectively.

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These values are smaller than those found for the dissociation of the contact $\sim S^-,Na^+$ ion pairs in the above solvents, namely, −60 and −63 eu, and larger than those characterizing the dissociation of the solvent-separated Na^+,BPh_4^- ion pairs, *i.e.*, 23 and 24 eu, respectively. This may indicate a lower degree of coordination of the free Cs^+ ion than that of Na^+ ion, a very plausible conclusion. However, one would expect $-\Delta S$ for $\sim S^-,Cs^+$ dissociation to be substantially larger in DME than in THF, and this is hardly the case. A similar situation is found for the dissociation of Cs^+,BPh_4^- ion pairs in these two solvents,[6] the respective $-\Delta S$ values being 32 and 33 eu. The dissociation constant of both cesium salts is about 20-fold smaller in THF than in DME (at 25°), but this change arises only from a decrease in the respective ΔH_{Diss}, ΔS_{Diss} being virtually constant. It is possible that the concept of two thermodynamically distinct ion pairs does not apply to these systems.[11,12]

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Spectroscopic Evidence for Ionic Processes of γ-Irradiated Alkyl Iodides at −196°[1]

Jai Pal Mittal[2] and William H. Hamill

Contribution from the Department of Chemistry and Radiation Laboratory,[3] University of Notre Dame, Notre Dame, Indiana 46556. *Received May 31, 1967*

Abstract: The optical absorption bands produced by γ irradiation of alkyl iodides in alkane matrices at −196° can be assigned to three species: 370 and 440 mμ, A; 390 and 480 mμ, B; 540 and 760 mμ, C. All are suppressed by positive charge traps, only B by electron traps. Isothermal relaxation in a soft matrix shows that A → B, A → C, and C → B. Only A appears initially at small RI, but all appear at large RI. Assignments are $A = RI^+$, $B = RI\cdot I$, $C = (RI)_2^+$. The ^2P states of RI^+ account for the separations of the A bands. Efficient formation of $RI\cdot I$ is attributed to ion recombination between RI^+ and I^-. The optically excited complex, RI^+I^-, has doublet character attributable to mixing of the ^2P states of RI^+, accounting for the B bands. Moreover, the known toluene and mesitylene (Ar) charge-transfer complexes with I were shown to form predictably from combination of Ar^+ with I^-. The assignment of C bands is supported semiquantitatively by previously reported excited states of persistent collision complexes of RI^+ and RI from mass spectrometry. These processes account for the major radiolytic effects. The formation of an identifiable charge-transfer complex $A\cdot C$ by recombination of C^+ and A^- provides the possibility, in suitable instances, of resolving a major mechanistic problem in radiation chemistry.

Repeated comparative studies of the photolysis and radiolysis of liquid alkyl iodides have shown limited similarities.[4] These are likely to arise principally from the weak C–I bond and geminate radical–atom interactions rather than from similarities of primary processes. A much better correlation was found between the results from radiolysis and ion–molecule reactions[5,6] but this may prove to be only a *tour de force*. Dissociative electron attachment of alkyl chlorides, bromides, and iodides in a hydrocarbon matrix at −196[7a] is consistent with their radiation chemistry at ~20°,[4,6] and similar studies support the interpretation that it can be a major radiolytic mechanism.[7b] The fates of the positive ions in liquid and solid alkyl iodides have not been determined, but recent work with γ-irradiated alkyl iodides in rigid matrices at −196° shows fairly complicated optical absorption spectra. These are due in part to positive ions and vary with concentration, with optical excitation, and with matrix relaxation.[8,9]

In a matrix of 3-methylpentane (3MP) both the electron and the (positive) hole migrate and are trapped by methyl iodide.[8] The sign of electric charge associated with a given species of color center, or with its precursor, can be inferred by the effect of tested additives. Thus, an additive known to trap holes depresses yields of positively charged color centers, and also enhances yields of anionic color centers by interfering with their destruction through charge recombination. Electron trapping additives operate analogously. Thus, the band at ~390 mμ from I_2, HI, CH_3I, and p-$C_6H_4I_2$ in 3MP following γ irradiation was depressed by CH_3Cl and attributed to I^-.[8] The 390-mμ band has since

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[2] Peter C. Reilly Fellow; on leave of absence from Bhabha Atomic Research Center, Trombay, Bombay, India.

[3] The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-536.

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