Reciprocal plots of the data were found to be linear, and Y and k_{24a}/k_{24b} could be obtained from the intercept and slope. Since the rate of k_{24b} is assumed to be independent of the fluorescer, the relative rates of the excitation step (24a) for various fluorescers can be determined from the k_{24a}/k_{24b} values.

In general, although there were a few exceptions, the rate of excitation increased as the ionization potential and excitation energy of the fluorescer decreased. It has been suggested that the excitation step involves initial formation of a charge-transfer complex between the intermediate and the fluorescer wherein the fluorescer acts as an electron donor.[26] If this is correct, the rate of excitation would increase as the ionization potential of the fluorescer decreased, in agreement with the experimental results.

As discussed earlier, the over-all yield of excited fluorescer can be determined by dividing the chemiluminescence quantum yield by the fluorescence quantum yield of the fluorescer. Thus Y divided by the appropriate fluorescence quantum yield gives, according to Chart III, the yield of 17 times the yield of excited fluorescer from 17 in step 24a. Since the yield of 17 should be independent of the fluorescer, the relative excitation yields in step 24a could be determined from the Y and fluorescence quantum yield values as a function of fluorescer structure. In general, the excitation yield was found to increase as the excitation energy of the fluorescer decreased. The result is thus in agreement with Eyring's suggestion that decreasing electronic excitation energy should favor the formation of electronic vs. vibrational excited states.[10] With low-energy fluorescers the over-all yield of excited fluorescer was found to approach 60%.

The experiments require that the fluorescer act as a catalyst for decomposition of the chemiluminescent intermediate. It has been suggested that a spontaneous concerted decomposition of 17 might be slow because of the low probability of a reaction which requires the conversion of substantial chemical energy to vibrational energy in small product molecules.[26] The fluorescer would then act as a catalyst by providing an energy acceptor. It should be noted, however, that concerted decomposition of a four-membered ring system such as 17 would be required to provide an excited product if it obeyed the Woodward–Hoffmann symmetry rule.[37,38] Excited singlet CO_2 requires an enthalpy change of 110 kcal or more[39] and the formation of two excited triplets (formation of a triplet pair would be required for spin conservation) would require at least as much. Thus concerted decomposition in conjunction with a fluorescer requiring 70 kcal mol^{-1} or less for excitation would be favored. Indeed decomposition of a charge-transfer complex between 17 and a fluorescer could provide a short-lived carbon dioxide–fluorescer mixed eximer[7] capable of dissociation to ground-state CO_2 and excited fluorescer.[21]

Our understanding of chemiluminescence remains incomplete, and it is likely that current mechanism proposals will require modification as further evidence becomes available. Current theories, however, have now made possible the successful design of new chemiluminescent reactions. Moreover, peroxyoxalate chemiluminescence has demonstrated that efficient nonenzymatic chemiluminescent reactions are possible.

(37) R. Hoffmann and R. B. Woodward, J. Am. Chem. Soc., 87, 2046 (1965); P. D. Bartlett, Science, 159, 833 (1968).

(38) F. McCapra, Chem. Commun., 155 (1968), has also suggested recently that the Woodward–Hoffmann rule may account for chemiluminescent reactions involving the decomposition of four-membered cyclic species.

(39) M. A. A. Clyne and B. A. Thrush, Proc. Roy. Soc. (London), A269, 404 (1962).

Ions and Ion Pairs

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While free ions are well known to all chemists, familiarity with ion pairs is less common. The concept of ion pair was introduced by Bjerrum[1] to account for the behavior of ionophores in solvents of low dielectric constant. Ionophores[2] are substances composed of ions which do not combine into covalently bonded molecules. What are, therefore, ion pairs? These were visualized as associates of two oppositely charged ions retaining their basic properties when bonded together by Coulombic forces and, to a lesser extent, by other interactions. Their electric neutrality makes them nonconducting and this was of paramount importance for Bjerrum.

The subject of ion pairs has been reviewed recently by this writer.[3] It was shown that the utility of this concept is lost when one deals with dense systems at elevated temperatures; e.g., it is unprofitable, and perhaps meaningless, to describe molten sodium chloride in terms of free ions and ion pairs. In dilute systems such a description is advantageous since the ions are either far apart from each other or coupled into pairs,

(1) N. Bjerrum, Kgl. Danske Videnskab Selskab, 7, No. 9 (1926).
(2) R. M. Fuoss, J. Chem. Educ., 32, 527 (1955).

(3) M. Szwarc, "Carbanions, Living Polymers and Electron-Transfer Processes," Interscience Publishers, New York, N. Y., 1968.

intermediate distances being improbable. Under those conditions, as pointed out by Ramsey,[4] the formation of ion pairs may be discussed in thermodynamic terms.

Contrary to Bjerrum's expectation, the pairing of ions often leads to the formation of new, thermodynamically distinct species possessing properties strikingly different from those of the free ions. Two examples illustrate this point.

(1) Many alkali salts are fully dissociated into free ions in hexamethylphosphoramide.[5] Thus, the reduction of quinoline, Q, with sodium yields in this solvent stable free quinoline radical anions, $Q\cdot^-$, and Na^+ cations.[6] In tetrahydrofuran the ions are paired and, in contradistinction to free ions, the pairs dimerize into covalently bonded diamagnetic dianions.
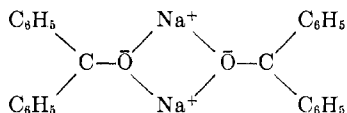
$$2(Q\cdot^-,Na^+) \rightleftarrows Na^+,^-Q-Q^-,Na^+$$
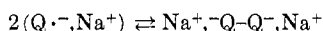
The equilibrium lies far to the right; even the sensitive esr technique can hardly detect $Q\cdot^-$ radical anions in this solvent. Nevertheless, the dimers dissociate quantitatively into radical ions when dissolved in hexamethylphosphoramide,[6] i.e., the equilibrium

$$2Q\cdot^- \rightleftarrows {}^-Q-Q^-$$
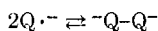
lies far to the left. A somewhat similar situation is encountered with radical anions of diphenylacetylene.[7]

A different type of dimerization is observed for ketyls.[8] Their ion pairs yield paramagnetic dimers bonded by electrostatic forces, e.g.

$$\begin{matrix} C_6H_5 & & Na^+ & & C_6H_5 \\ & \diagdown & & \diagup & \\ & C-\bar{O} & & \bar{O}-C & \\ & \diagup & & \diagdown & \\ C_6H_5 & & Na^+ & & C_6H_5 \end{matrix}$$
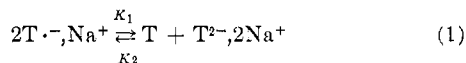
as well as the covalently bonded diamagnetic pinacolates.

(2) Radical anions may disproportionate into neutral species and dianions, e.g., the radical anions of tetraphenylethylene, $T\cdot^-$, yield the hydrocarbon, T, and its dianion, T^{2-}. Three distinct equilibria are observed. In hexamethylphosphoramide only the free ions exist, and the equilibrium is given by

$$2T\cdot^- \overset{K_3}{\rightleftarrows} T + T^{2-}$$
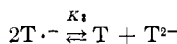
K_3 being very small,[9] about 10^{-4}. In tetrahydrofuran at room temperature the ion pairing is extensive, although the concentration of the free $T\cdot^-$ ions and of T^{2-},Na^+ is not negligible. The disproportionation is governed then by equilibria 1 and 2, i.e.

$$2T\cdot^-,Na^+ \overset{K_1}{\underset{K_2}{\rightleftarrows}} T + T^{2-},2Na^+ \tag{1}$$

Figure 1. van't Hoff plots of the dissociation constants of ionic agglomerates. Upper line: $T\cdot^-,Na^+ \rightleftarrows T\cdot^- + Na^+$ in THF, $K_{diss,1}$. Note the low value of $-\Delta H_1$, $K_{diss,1} = 100 \times 10^{-6}$ M at 20°. Lower line: $T^{2-},2Na^+ \rightleftarrows T^{2-},Na^+ + Na^+$ in THF, $K_{diss,2}$. Note the high value of $-\Delta H_2$, $K_{diss,2} = 0.8 \times 10^{-6}$ M at 20°.
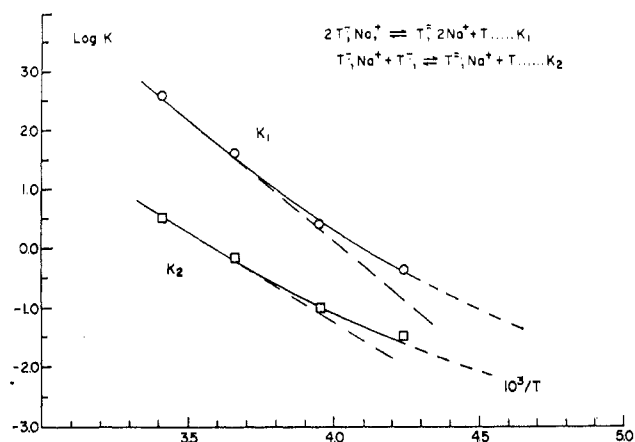
Figure 2. van't Hoff plots of the disproportionation constants of radical anions of tetraphenylethylene. Upper line: $2T\cdot^-,Na^+ \rightleftarrows T + T^{2-},2Na^+$, $K_1 = 400$ at 20°. Lower line: $T\cdot^- + T\cdot^-,Na^+ \rightleftarrows T + T^{2-},Na^+$, $K_2 = 3.3$ at 20°.

$$T\cdot^- + T\cdot^-,Na^+ \rightleftarrows T + T^{2-},Na^+ \tag{2}$$
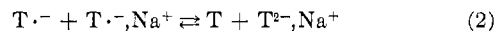
and the ratio $K_1/K_2 = K_{diss,1}/K_{diss,2}$. The constants $K_{diss,1}$ and $K_{diss,2}$ refer to

$$T\cdot^-,Na^+ \rightleftarrows T\cdot^- + Na^+ \quad (K_{diss,1})$$

and

$$T^{2-},2Na^+ \rightleftarrows T^{2-},Na^+ + Na^+ \quad (K_{diss,2})$$
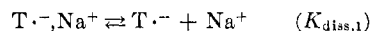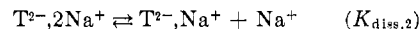
respectively, and their values were determined conductometrically. The results[9] are presented in Figure 1; further dissociation of T^{2-},Na^+ into $T^{2-} + Na^+$ is negligible under these conditions, making the contribution of equilibrium 3 insignificant.

$$2T\cdot^- \overset{K_3}{\rightleftarrows} T + T^{2-} \tag{3}$$

Spectrophotometric studies combined with conductometric investigations led to the constants K_1 and K_2, the respective values being given in Figure 2. At 20° $K_1 = 400$ and $K_2 = 3.3$, indicating that the pairing of sodium ions with T^{2-} is more profitable than their association with $T\cdot^-$.

Disproportionation of free radical anions is probably endothermic; crowding of two extra electrons in one

(4) J. T. Denison and J. B. Ramsey, J. Am. Chem. Soc., **77**, 2615 (1955).

(5) S. N. Bhadani, J. Jagur-Grodzinski, and M. Szwarc, unpublished results.

(6) J. Chaudhuri, S. Kume, J. Jagur-Grodzinski, and M. Szwarc, J. Am. Chem. Soc., **90**, 6421 (1968).

(7) A. Cserhegyi, E. Franta, J. Chaudhuri, J. Jagur-Grodzinski, and M. Szwarc, ibid., **89**, 7129 (1967).

(8) N. Hirota and S. I. Weissman, ibid., **86**, 2538 (1964).

(9) R. C. Roberts and M. Szwarc, ibid., **87**, 5542 (1965); A. Cserhegyi, J. Jagur-Grodzinski, and M. Szwarc, ibid., in press.
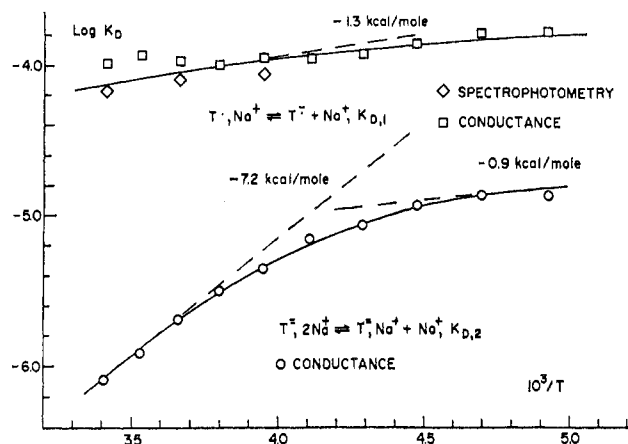
molecule leads to repulsion which is only partially balanced by the greater (physical) solvation energy of the T^{2-} anion. The entropy of disproportionation is small, hence the process is unfavorable as indicated by the low value of K_3. The disproportionation of ion pairs is also endothermic as shown by Figure 2. The polar molecules of solvent interact stronger with $T\cdot^-,Na^+$ dipoles than with the quadrupoles, $T^{2-},2Na^+$. Hence, $-\Delta H_1 > -\Delta H_3$, and a similar argument implies that $-\Delta H_2$ should have an intermediate value. However, the disproportionation substantially increases the entropy of the system: the solvent molecules are more orderly arrayed around a dipole, $T\cdot^-,Na^+$, than in the vicinity of a quadrupole, $T^{2-},2Na^+$. Moreover, as we shall see, the molecules of tetrahydrofuran form a rigid shell around the Na^+ ion in $T\cdot^-,Na^+$ pair but not in $T^{2-},2Na^+$. Thus, the gain in entropy more than balances the loss of energy, making $K_1 > K_2 \gg K_3$. The favorable disproportionation of $T\cdot^-,Na^+$ ion pairs in tetrahydrofuran is driven, therefore, by the increase of entropy and not by the decrease in energy.

The Role of Solvent in the Formation of Ion Pairs

Let us return to the basic problem of ion-pair formation and consider univalent ions and their ion pairs imbedded in a hypothetical *continuous, structureless* but polarizable medium. The dielectric constant, D, of such a "solvent" is temperature *independent*, and the presence of ions, or ion pairs, does not induce any degree of order in this idealized liquid.[10] The dissociation constant, K_{diss}, of ion pairs is given by

$$-RT \ln K_{diss} = \Delta E_{diss} - T\Delta S_d$$

$$= \underset{\substack{\text{electrostatic} \\ \text{binding}}}{e^2/D(r_1 + r_2)} + \underset{\substack{\text{binding arising} \\ \text{from other forces}}}{\text{(BD)}}$$

$$- T\Delta S_d$$

where $\Delta E_{diss} \approx \Delta H_{diss}$ is the energy of dissociation, ΔS_d is the standard entropy of dissociation per ion pair, r_1 and r_2 are the radii of the ions treated, for the sake of simplicity, as charged spheres, and (BD) is the binding energy of the pair due to forces other than Coulombic. Calculation of ΔS_d is straightforward, *e.g.*, it is outlined explicitly on p 231 of ref 3.

Real solvents differ from the idealized medium. They have discrete molecular structure and often dipolar properties. Their molecules perform an endless Brownian dance, its vigor increasing with temperature. The Brownian motion destroys, at least partially, their expected orderly arrangement making the dielectric constant of a real solvent temperature *dependent*. Usually its value decreases with rising temperature, although if polar solvent molecules are associated into less polar aggregates a reverse trend may be observed.

Ions and ion pairs imbedded in such a medium orient solvent molecules, albeit their orientation is continu-

ously perturbed by Brownian motion. The degree of orientation is greater around free ions than in the vicinity of ion pairs, and hence the dissociation of ion pairs into free ions decreases the entropy of the system. To a first approximation[4] the entropy change, ΔS_m, is given by

$$\Delta S_m = \{e^2/DT(r_1 + r_2)\}(\partial \ln D/\partial \ln T)$$

<div align="right">ergs/mole degree</div>

if neither r_1 and r_2 nor (BD) are temperature dependent. Consequently, a new and usually large term, $-T\Delta S_m$, contributes now to the free energy of dissociation. This term represents the free energy stored in the medium, and consequently $\Delta E_{diss} \approx \Delta H_{diss}$ is

$$\Delta H_{diss} = \{e^2/D(r_1 + r_2)\}(1 + \partial \ln D/\partial \ln T) + \text{(BD)}$$

For many solvents $\partial \ln D/\partial \ln T < -1$, and then the dissociations may be exothermic. For example, if $D = 8$, $\partial \ln D/\partial \ln T = -1.15$, $r_1 + r_2 = 10$ Å, and (BD) ≈ 0, then $\Delta S_m = -16$ eu and $\Delta H_{diss} \approx -2$ kcal/mol.

The dissociation process may be visualized in mechanical terms as a movement of a representative point on a potential energy surface (or curve). The distance r separating the ions is the reaction coordinate, and the potential energy is given by the sum of Coulombic energy (e^2/Dr) and the binding energy (BD) (r). The thermodynamically derived ΔE_{diss} or ΔH_{diss} is inappropriate and misleading if applied to such a model because the free energy stored in the medium $(-T\Delta S_m)$ is then disregarded. The above potential energy curve is different for different solvents because their nature determines the dielectric constant. By the same token, the potential energy curve varies with temperature.

Let us restate the last argument. The energy of two ions imbedded in a solvent and separated by a distance r depends on the *average* configuration of the surrounding molecules. The *average* varies with temperature, and thus the potential energy curve becomes a function of temperature. Indeed, a solvent at two different temperatures provides, after all, two different media. One may say, with some justification, that the content of a bottle filled with a solvent varies with its temperature; only the label on the container remains the same.

The simple treatment is adequate when the ions are substantially larger than the surrounding solvent molecules, but further sophistication is needed when the ions are small. The ion-quadrupole interaction,[11] superimposed upon ion-dipole interaction, affects cations and anions in a different way. Partial dielectric saturation decreases the microscopic dielectric constant of the medium in the vicinity of small ions.[12] The most important, however, are the phenomena caused by the nonspherical symmetry of solvent molecules.[13] For example, the dipole of the tetrahydrofuran molecule is due, mainly, to the lone pairs of electrons on the oxygen

(10) Solvents for which the static dielectric constant is equal to n^2 (n = refractive index) show this behavior.

(11) A. D. Buckingham, *Discussions Faraday Soc.*, **24**, 151 (1957).
(12) See ref 3, p 238.
(13) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

atom. Hence, cations interact with this ether stronger than anions (see Figure 3). One concludes that the purely *physical*, nonstoichiometric solvation, given by the Born term, $(e^2/2r)(1 - 1/D)$, is not sufficient to describe the interaction of solvent molecules with ions or ion pairs. A more powerful interaction combined with steric restrictions often leads to stoichiometric associations referred to as *chemical* solvation. Its degree is different for a free ion and for an ion pair, and thus additional energy and entropy terms contribute to the free energy of ion-pair dissociation. The distinction between the physical and chemical solvations is not rigorous and sometimes is ambiguous; nevertheless, it is useful and revealing. Therefore, this terminology will be maintained for didactic purpose.

The first evidence for the existence of ion pairs was obtained from conductance studies; however, observations of other physical properties provided even better proof for their presence. The uv or visible spectrum of an absorbing ion often shows a hypsochromic shift when the free ion is paired because the interaction of a cation with an anion is usually stronger in the ground state than in the excited state. The pairing leads also to a new kind of vibration, cation oscillating relative to anion, and the relevant ir bands have been observed.[14] The most striking changes are observed in the esr spectra of radical anions as they are paired with cations, e.g., each hyperfine line of the esr spectrum of the free naphthalenide radical ion appears as a quadruplet in the spectrum of its sodium ion pair.[15] The splitting, resulting from the interaction of the odd electron with the spin of the Na^+ nucleus, provides the strongest and most direct evidence for the existence of ion pairs as truly independent species. In fact, studies of the esr spectra led to information about the lifetime of ion pairs, their vibration, and structure.

Structure of Ion Pairs

Ions may strongly interact with neighboring molecules and surround themselves with rigid solvation shells (chemical solvation) which affect their Stokes radii. The intrinsically small Na^+ ion (crystal radius 0.95 Å) has a Stokes radius of 4 Å in tetrahydrofuran, whereas the Stokes radius of the large Cs^+ ion is 2.4 Å, being only slightly larger than its crystal radius.[16] A small ion generates in its vicinity a more powerful field than a large ion; hence, the former, but not the latter, may produce a rigid solvation shell in some media. The formation of a shell is opposed by the loss of translational entropy of the solvent molecules immobilized around the ion. In tetrahydrofuran probably four molecules of the ether form the solvation shell of Na^+. The polarizing field of the Cs^+ ion is too
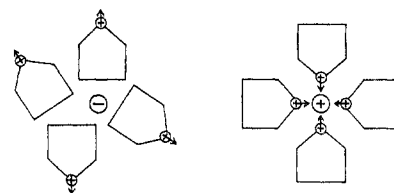

Figure 3. Organization of tight solvation shell of THF molecules around cation and a partial polarization of the solvent molecules around anion.

weak to cope with such a large loss of translational entropy, and therefore Cs^+ is not surrounded by a tight solvation shell in tetrahydrofuran. A different situation is encountered in dimethoxyethane.[16b] This ether acts as a bidentate agent; only two of its molecules are needed to achieve the degree of coordination produced by four molecules of tetrahydrofuran. Consequently, even the large Cs^+ ion forms a tight solvation shell in this medium; thus the Stokes radii of Cs^+ and Na^+ ions in dimethoxyethane are 3.6 and 3.4 Å, respectively.

The association of an ion surrounded by a tight solvation shell with its counterion proceeds smoothly until the shell comes into contact with the partner. At this stage either the structure of the pair separated by solvent molecules is preserved or the solvation shell is squeezed out in a discontinuous process leading to a contact pair. Such two-step associations have been revealed by various relaxation experiments.[17]

The above discussion implies that two, or more, types of ion pairs may coexist in solution, each being characterized by its own physical and chemical properties.[18] However, the simultaneous coexistence of different types of ion pairs is only possible in a medium endowed with discrete molecular structure. Such a situation is impossible and meaningless in a hypothetical *continuous* solvent.

Ions which weakly interact with the solvent and do not surround themselves with tight solvation shells form contact pairs only. This situation is encountered in poorly solvating liquids or for bulky ions. Those that strongly interact with solvent molecules tend to form solvent-separated pairs, especially when combined with large counterions.[9] Let us clarify the last point. An ion of radius r_1 surrounded by a tight solvation shell of thickness Δr_1 combines with another having radius r_2. The conversion of the resulting solvent-separated pair into a contact pair releases Coulombic energy

$$\sim (e^2/D)\,\Delta r/(r_1 + r_2 + \Delta r)(r_1 + r_2)$$

This "driving force" decreases with increasing r_2 for constant r_1 and Δr. Thus, a sodium salt of a small anion forms contact pairs in tetrahydrofuran while solvent-separated pairs are produced if the anion is bulky.[9]

(14) W. F. Edgell, A. T. Watts, J. Lyford, and W. M. Risen, *J. Am. Chem. Soc.*, **88**, 1815 (1966).

(15) (a) F. C. Adam and S. I. Weissman, *ibid.*, **80**, 1518 (1958); (b) N. M. Atherton and S. I. Weissman, *ibid.*, **83**, 1330 (1961).

(16) (a) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 608 (1965); (b) C. Carvajal, K. J. Tölle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **87**, 5548 (1965); (c) D. Nicholls, C. Sutphen, and M. Szwarc, *J. Phys. Chem.*, **72**, 1021 (1968).

(17) (a) H. Diebler and M. Eigen, *Z. Phys. Chem.* (Frankfurt), **20**, 299 (1959); (b) M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 107 (1962).

(18) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *J. Am. Chem. Soc.*, **76**, 2597 (1954).

The discrete molecular structure of the solvent affects the shape of the pseudo potential energy curve describing the dissociation process. As the two bare ions are pulled apart the resulting empty space cannot accommodate solvent molecules until the separation is sufficiently large, because solvent molecules have a finite size.[19] The curve may acquire, therefore, a shape shown in Figure 4A, the second minimum appearing at the distance at which a solvent molecule may be squeezed in. The two minima correspond to two distinct species coexisting in equilibrium. This description, however useful, is oversimplified.[20] The pseudo potential curve is temperature dependent; the *average* configuration of the surrounding solvent molecules affects the energy of a pair separated by distance r. The steep maximum shown in Figure 4 may appear at one temperature but not at another. In brief, the model, originally proposed by Grunwald,[19] is static in nature. The potential energy is assumed to be uniquely determined by the interionic distance, r, while in reality the ion pair is imbedded in a fluctuating environment, its properties varying with temperature. For deep and narrow potential wells, the concept of contact and solvent-separated pairs as two thermodynamically distinct species is justified within a relatively wide temperature range. For wide and shallow wells, shown in Figure 4B, C, the distinction may become meaningless.[21] The well may change its shape, being like Figure 4B at low temperature and like Figure 4C at high. The pairs are then gradually transformed from a contact into a solvent-separated type as the temperature rises, and the concept of two *thermodynamically* distinct species does not apply to these systems (see, *e.g.*, ref 3, pp 253–264).

Physical and Chemical Evidence for Two Types of Ion Pairs

Various observations provide evidence for two, or more, types of ion pairs. The first physical evidence for ion pairs was reported by Weissman,[15] who resolved the hyperfine lines of the esr spectrum of sodium naphthalenide into quadruplets. The splitting is caused by the pairing of $C_{10}H_8 \cdot^-$ with Na^+ ions, and its relatively large magnitude (about 1 G) indicates a rather close proximity of the sodium ion to the naphthalene framework. Unsplit lines were observed simultaneously with the quadruplets and the latter were attributed to the free $C_{10}H_8 \cdot^-$ ions. However, the conductance studies of these solutions[20] prove that the concentration of the free ions is too low to account for the reported intensities, and therefore the single lines manifest the presence of solvent-separated pairs. The splitting constant decreases on separation of the ions and the quadruplet may appear then as a single line. Subsequent studies of Hirota[22] revealed the presence of more than two

(19) E. Grunwald, *Anal. Chem.*, **26**, 1696 (1954).
(20) P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, **70**, 3180 (1966).
(21) R. V. Slates and M. Szwarc, *J. Am. Chem. Soc.*, **89**, 6043 (1967).
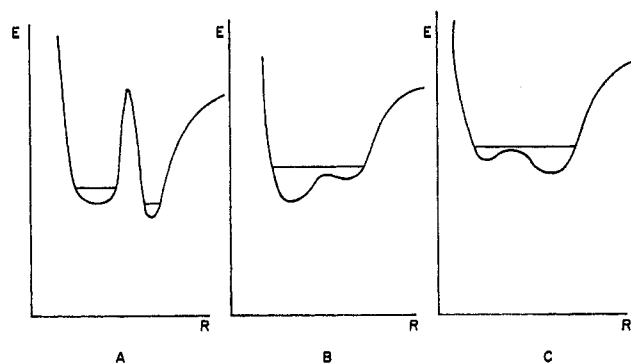(22) N. Hirota, *J. Phys. Chem.*, **71**, 127 (1967).

Figure 4. Pseudo potential energy curves of an ion pair in a solvent as a function of the interionic distance.

types of ion pairs and showed that the pertinent equilibrium constants may be determined from esr data.

As the contact pair is transformed into a solvent-separated one, a bathochromic shift is observed in their uv and visible absorption spectra. This phenomenon was successfully utilized in our laboratory by Hogen–Esch and Smid[23] to determine the equilibrium constant of the ion-pair solvation. Extension of this work[24] showed that the ability of solvents to separate the ions of a pair depends on various factors (constitutional and steric) and not merely on the dielectric constant. The ability of an ether to solvate alkali ions is often correlated with its basicity, indicating that a sort of a bond is established between the cation and the oxygen atom of the solvating molecule.

Useful information about the structure of the ion pair is derived from conductance studies. The dissociation of $\sim S^-, Na^+$ ion pairs of living polystyrene in tetrahydrofuran is strongly exothermic, $-\Delta H_{diss} = 8$ kcal/mol, while the relevant exothermicity of $\sim S^-, Cs^+$ is less than 2 kcal/mol (see Figure 5a, b). The free Na^+ ion, but not the Cs^+, is surrounded by a tight solvation shell in tetrahydrofuran. Hence, the above results are explicable if both ion pairs are of contact type, *i.e.*, both being poorly solvated. The chemical solvation of the free Na^+ ion formed on dissociation provides then additional gain for the process, increasing the dissociation constant and the $-\Delta H_{diss}$ of $\sim S^-, Na^+$. Such a gain is not provided by the dissociation of $\sim S^-, Cs^+$; thus, the respective K_{diss} and $-\Delta H_{diss}$ are low.

Figure 5a, b contrasts with Figure 1 which represents the van't Hoff plots for the dissociation of $T \cdot^-, Na^+$ and $T^{2-}, 2Na^+$ in tetrahydrofuran. Both processes yield tightly solvated Na^+ ions; K_{diss} for $T \cdot^-, Na^+$ is high, although $-\Delta H_{diss}$ is low, whereas the equilibrium constant of the dissociation of $T^{2-}, 2Na^+$ into $T^{2-}, Na^+ + Na^+$ is low in spite of the high exothermicity of this process. The bulkiness of the $T \cdot^-$ radical ion prevents the formation of contact pairs; thus, $T \cdot^-, Na^+$ retains the structure of a well-solvated solvent-separated pair. The skewed shape of T^{2-} makes it possible to bring

(23) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307 (1966).
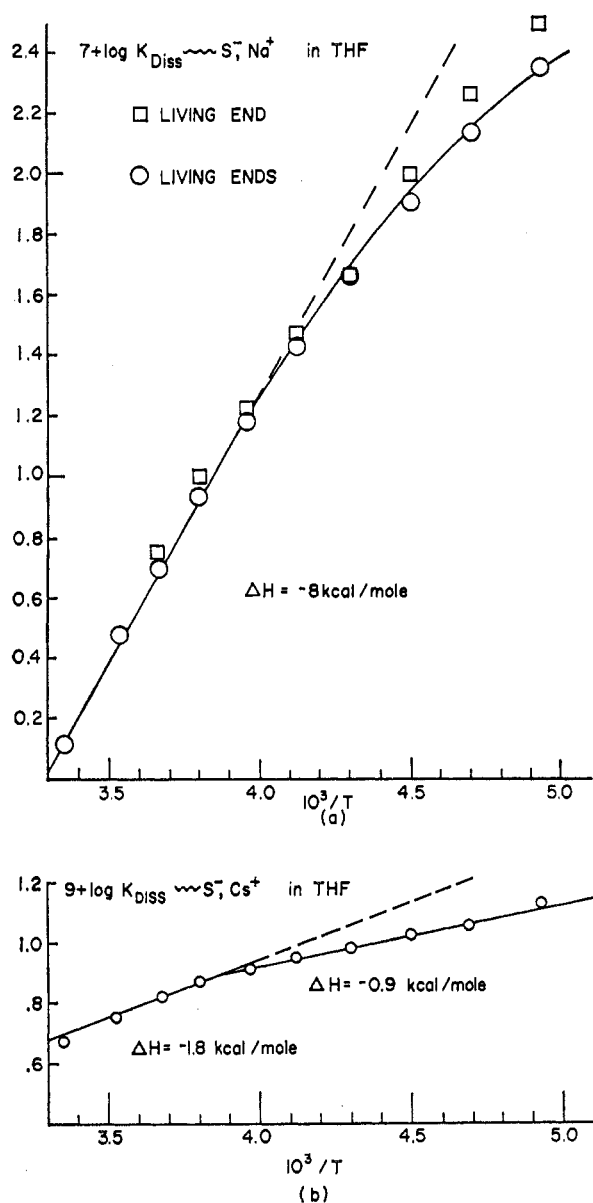(24) L. L. Chan and J. Smid, *ibid.*, **90**, 4654 (1968).

Figure 5. van't Hoff plot for the dissociation of living polystyrene salts in THF. (a) The dissociation of the sodium salt, K_{diss} and $-\Delta H_{diss}$ high. (b) The dissociation of the cesium salt, K_{diss} and $-\Delta H_{diss}$ low.

closely together the ions in $T^{2-},2Na^+$ and form a tight poorly solvated aggregate.[9] Thus, $T\cdot^-,Na^+$ easily dissociates but no additional heat is produced in the process, whereas the dissociation of the tight $T^{2-},2Na^+$ is difficult, but it produces much heat due to solvation of the resulting free Na^+ ions.

Solvation of Ion Pairs by External Agents. Isomeric Ion Pairs

A suitable agent, E, added to a solution of ion pairs may produce a new ionic species, and equilibria such as

$$A^+,B^- + E \rightleftarrows A^+,B^-(E)$$

$$A + E \rightleftarrows A^+(E)$$
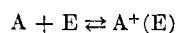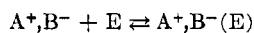
are then established. Association of ion pairs with complexing agents permits us to investigate two problems: (a) how the nature of the complexing agent affects the

equilibrium of the adduct formation, and especially to what extent the heat and the entropy of association are influenced by its structure; (b) the complexing agent may be treated as a probe with the aid of which the structure of the original ion pair could be studied. For example, a contact ion pair may interact strongly with the surrounding solvent molecules and form on its periphery a relatively rigid coordination shell. A powerful coordinating polydentate agent added to such a solution would replace two or more solvent molecules in the shell. *Increase* in the entropy of the system coupled with low exothermicity of the process provides a diagnostic evidence for the proposed structure of the original pair. A similar reaction involving a contact ion pair which is poorly solvated should *decrease* the entropy of the system.

How can such reactions be studied? A few examples will illustrate the possible approaches to this problem.

Biphenyl, B, like other aromatic hydrocarbons, reacts with metallic sodium and the following equilibrium is eventually established.

$$\text{metallic Na} + \text{B (solution)} \rightleftarrows B\cdot^-,Na^+ \text{ (solution)}$$
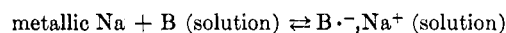
The equilibrium constant, K_B, may be determined spectrophotometrically over a wide temperature range (see, e.g., Figure 6), and the results[21,25] permit us to calculate the pertinent thermodynamic quantities such as ΔH_B and ΔS_B. The equilibrium constant, K_B, and the heat of the reaction are profoundly affected by the solvent. The shape of the solvent molecules plays an important role in the process, e.g., at $0°$ K_B was found to be 5.0 in 1,2-dimethoxypropane but only 0.04 in 1,3-dimethoxypropane.[25]

Addition of diglyme or triglyme to the equilibrated solution increases the concentration of $B\cdot^-$ radical ions[21] (see again Figure 6) because a new equilibrium (K_G), viz.

$$Na^+,B\cdot^- + n \text{ glyme} \rightleftarrows Na^+,B\cdot^-(\text{glyme})_n$$
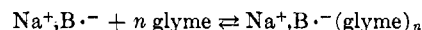
is established in the system and consequently further reaction between sodium and biphenyl has to take place to replenish the "ordinary" $Na^+,B\cdot^-$ pairs consumed by the glymation. It may be shown that

$$K_G[\text{glyme}]^n = (K_{ap} - K_B)/K_B$$

where K_{ap} denotes the ratio [total $B\cdot^-$]/[B]. The experimental results led, therefore, to values of K_G at various temperatures and proved that $n = 1$.

The addition of diglyme does not affect the visible spectrum of $B\cdot^-,Na^+$ pairs; apparently this glyme becomes associated with the periphery of the pair without separating the ions. However, a small but unmistakable change in the spectrum is noted on the addition of triglyme; at any temperature two equally intense peaks appear, one at 400 mμ the other at 407 mμ, when an appropriate amount of triglyme is added.

(25) (a) A. I. Shatenstein, E. S. Petrov, and M. I. Belousova, "Organic Reactivity." Vol. 1, Tartus State University, Estonia, U.S.S.R., 1964, p 191; *Dokl. Akad. Nauk SSSR*, **161**, 889 (1965); (b) A. I. Shatenstein, E. S. Petrov, and E. A. Yakovleva, *J. Polymer Sci.*, C, **16**, 1729 (1967).
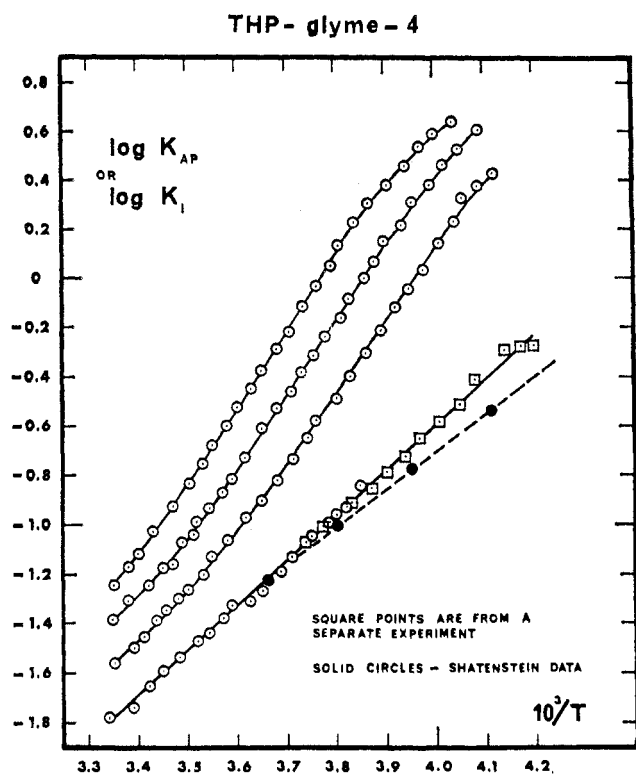
Figure 6. van't Hoff plot for K_B and K_{ap}. The system: metallic sodium + biphenyl (B) in solution $\rightleftarrows$ B·$^-$,Na$^+$, K_B, in the presence and absence of triglyme; solvent tetrahydropyran.

The former, observed also in the absence of glyme, is attributed to the contact or to the peripherally "glymated" pairs; the latter reveals the presence of the separated pairs. The extinction coefficients of both pairs seem to be identical; hence, only 50% of all the pairs are present as separated pairs when the peaks are equally intense. However, the calculation showed that at this stage 80% of the pairs were associated with triglyme. Therefore, 20% of the pairs are present in this system as the ordinary B·$^-$,Na$^+$ pairs, 30% form the pheripherally solvated B·$^-$,Na$^+$,(glyme) ion pairs, and 50% are present as the separated B·$^-$,(glyme),Na$^+$ pairs. Here we encounter an isomerism of ion pairs arising from the different location of the solvating agent. The heat and entropy change of this isomerization were determined.[21]

Separation of ions in tight sodium naphthalenide pairs takes place on the addition of minute amounts of tetraglyme to their tetrahydropyran solution. As seen in Figure 7, the 1.2-G esr sodium splitting constant of the original solution abruptly decreases to 0.38 G when $10^{-1} M$ tetraglyme is present.[26] When bothl ines appear in the spectrum their intensities and shape permit us to calculate the equilibrium constant and the relaxation time of the reaction N·$^-$,Na$^+$ + glyme $\rightleftarrows$ N·$^-$,(glyme), Na$^+$. The rate of collapse of the glymated pair is at most 5×10^6 sec^{-1}.

The equilibrium constant of the reaction

fluorenyl$^-$,M$^+$+solvating agent $\rightleftarrows$ fluorenyl$^-$(solvating agent),M$^+$

(26) K. Höfelmann, J. Jagur-Grodzinski, and M. Szwarc, in the course of publication.
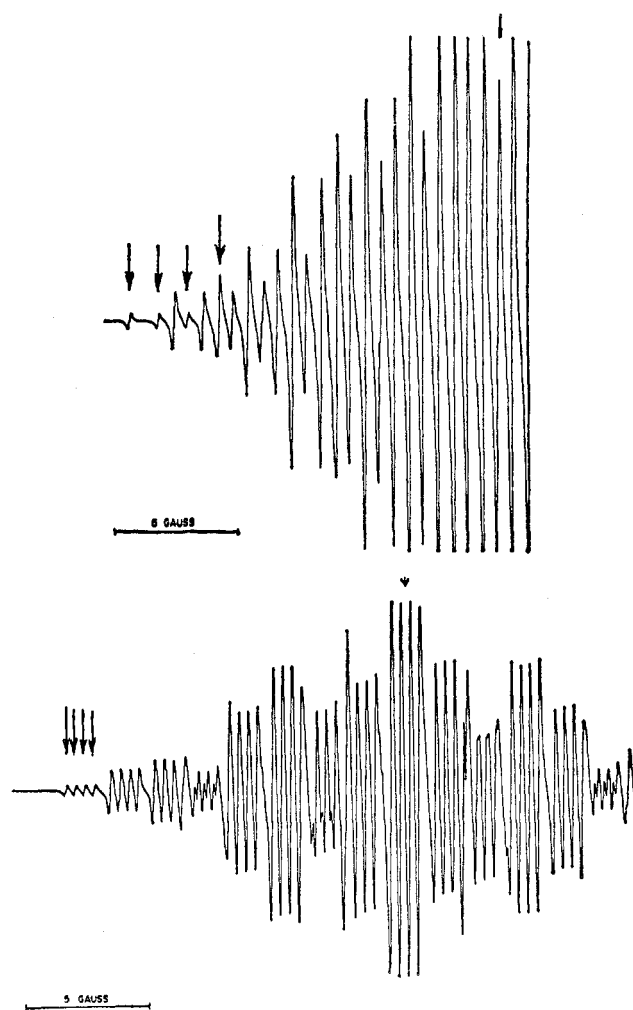

Figure 7. Esr spectra of sodium naphthalenide in tetrahydropyran in the absence (upper) and in the presence (lower) of tetraglyme. Note the large sodium splitting constant in the upper and low constant in the lower spectrum.

was investigated spectrophotometrically.[27] The contact pair absorbs at 345 mμ; the agent separated, formed on the addition of minute amounts of the solvating agent, at 371 mμ. These studies led to correlation of the structure of the agent with its capacity to separate the ion pair.

Replacement by glyme of an original solvent molecule separating a pair was also demonstrated. The nmr spectrum of the solvent, e.g., tetrahydrofuran, is shifted downfield by dissolved lithium fluorenyl because solvent molecules trapped between the ions experience different magnetic environment than those in the bulk. Addition of glyme moves the nmr lines of the solvent to their original position while the nmr spectrum of the glyme is shifted downfield.[27]

Propagation of Anionic Polymerization

Studies of anionic polymerization revealed many interesting details of kinetics of processes involving free ions, ion pairs, solvent-separated ion pairs, and

(27) L. L. Chan and J. Smid, J. Am. Chem. Soc., 89, 4547 (1967).

ion pairs solvated by external agents. The anionic polymerization of styrene, S, in tetrahydrofuran proceeds according to the equation

$$\underset{n \text{ units}}{\text{\textasciitilde}S^-,M^+} + S \xrightarrow{k_p} \underset{n+1 \text{ units}}{\text{\textasciitilde}S^-,M^+}$$
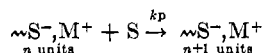
The absolute rate constant, k_p, was determined,[28,29] viz., $k_p = -(d \ln [S]/dt)/[\text{\textasciitilde}S^-,M^+]$. Here $[\text{\textasciitilde}S^-,M^+]$ denotes the concentration of the salt of growing polystyryl anions (living polymers) which is constant in each run because neither initiation nor termination takes place during an experiment. The observed k_p was found to increase with decreasing concentration of growing polystyrene, $[LP]$, namely, k_p is linear with $[LP]^{-1/2}$ as shown in Figure 8, the slopes and intercepts being different for the lithium, sodium, potassium, rubidium, and cesium salts. These results suggest that a minute proportion of the polystyryl salt is present in the form of free $\text{\textasciitilde}S^-$ ions, the latter propagating faster than the $\text{\textasciitilde}S^-,M^+$ ion pairs. If f is the fraction of the free $\text{\textasciitilde}S^-$ ions present in the reacting solution, and k_- and $k_\pm$ are the propagation constants of $\text{\textasciitilde}S^-$ and $\text{\textasciitilde}S^-,M^+$, respectively, then

$$k_p = fk_- + (1-f)k_\pm$$

The ratio $f^2/(1-f) = K_{diss}/[LP]$, where K_{diss} refers to

$$\text{\textasciitilde}S^-,M^+ \rightleftarrows \text{\textasciitilde}S^- + M^+ \qquad (K_{diss})$$

For small f the approximation $f = (K_{diss}/[LP])^{1/2}$ is valid. Thus

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

The slopes of the lines shown in Figure 8 are positive, i.e., $k_- > k_\pm$. This is not a trivial finding.[30] A free ion, which generates a more powerful field than an ion pair, is expected to be more reactive if the field polarization of the approaching monomer provides an important driving force for the reaction. However, if a "push-pull" mechanism operates, $\text{\textasciitilde}S^-$ polarizing one end of the monomer and M^+ the other, then a reverse order of reactivities could prevail.

The retarding effect of added salts sharing a common cation with the living polymers confirms the proposed mechanism of propagation. For example, the addition of sodium tetraphenylboride decreases the observed rate constant of sodium polystyryl polymerization;[29] the observed k_p is then a linear function of $1/[Na^+]$, as shown in Figure 9. Since $f = K_{diss}/[Na^+]$, $k_p = k_\pm + (k_- - k_\pm)K_{diss}/[Na^+]$. Virtually all the sodium ions are formed by the dissociation of the boride; their concentration could be calculated because the relevant dissociation constant is known[16] (the knowledge of the dissociation constant, K_{diss}, of $\text{\textasciitilde}S^-,M^+$ is not required).

The retardation experiments provide reliable propagation constants, $k_\pm$, of ion pairs (compare Figures 8 and 9); the pertinent data are given in Table I. Moreover, the ratio of the slopes of the lines shown in Figures

(28) C. Geacintov, J. Smid, and M. Szwarc, J. Am. Chem. Soc., 84, 2508 (1962).
(29) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, J. Phys. Chem., 69, 612 (1965).
(30) M. Szwarc, Makromol. Chem., 35A, 123 (1960).

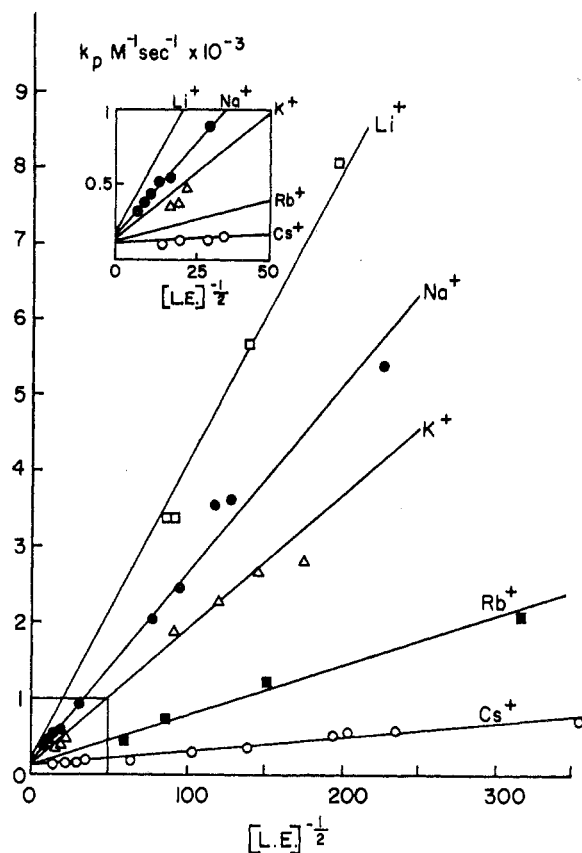Figure 8. Linear dependence of the observed propagation constant, k_p, of living polystyrene polymerization on [living polymers]$^{-1/2}$, for Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ salts in THF at 25°.

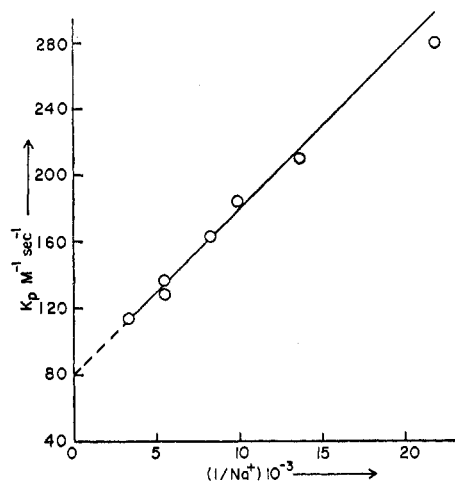Figure 9. Linear dependence of the observed propagation constant, k_p, of sodium polystyrene polymerization on $1/[Na^+]$. Sodium ions formed by the dissociation of Na$^+$,B(Ph)$_4$$^-$, in THF at 25°.

9 and 8 gives $K_{diss}^{1/2}$. Thus, the dissociation constants can be determined from the kinetic data, and the relevant values have been confirmed by conductometric studies.[29,31] Having K_{diss}, we can calculate the absolute value of the propagation constant of the free $\text{\textasciitilde}S^-$ ions, viz., k_- is $65000M^{-1}$ sec^{-1} at 25°, i.e., under these conditions the free $\text{\textasciitilde}S^-$ anion is 800 times more

(31) T. Shimomura, K. J. Tölle, J. Smid, and M. Szwarc, J. Am. Chem. Soc., 89, 796 (1967).

reactive as the $\sim\!\!S^-,Na^+$ ion pair.

The reactivity of the free $\sim\!\!S^-$ ions is only slightly influenced by the nature of the solvent. Only minor variations are observed in the relevant rate constants and activation energies when the polymerization is carried out in dimethoxyethane, tetrahydrofuran, tetrahydropyran, and methyltetrahydrofuran and in various mixtures of tetrahydrofuran with dioxane or benzene. Obviously, the anion does not interact strongly with these solvents.

Table I

Solvent	Li^+	Na^+	K^+	Rb^+	Cs^+
Living Polystyrene Salts					
Dioxane	0.9	3.4	20	21.5	24.6
		6.5	28	34	15
Benzene (nonassociated)			38	19	14
Tetrahydropyran	$<10^a$	14, 12^a 10	73	83	53
2-Methyltetra-hydrofuran	57	11	7.5		22
Tetrahydrofuran	~160	80	~100 (?)	50	25
Dimethoxyethane		3600			~150
Living Poly-α-methylstyrene Salts					
Dioxane		0.02	0.1	0.06	
Tetrahydropyran	2.6	0.047	0.25	0.35	0.26
Tetrahydrofuran		0.04			

Top header: $k_\pm$, l. mol^{-1} sec^{-1}

^{a} Aging the solution inhibits the reaction making $k_\pm$ smaller.

The situation is different for ion pairs, e.g., at 25° the $k_\pm$ of the sodium ion pair is about 4 M^{-1} sec^{-1} in dioxane, 80 M^{-1} sec^{-1} in tetrahydrofuran, and 3600 M^{-1} sec^{-1} in dimethoxyethane. Furthermore, because the pair involves a cation, its reactivity is affected by the cation's nature. In tetrahydrofuran the lithium ion pair is the most reactive in polymerizing styrene ($k_\pm \sim$ 150 M^{-1} sec^{-1} at 25°), while the cesium ion pair is the least reactive ($k_\pm \sim 25$ M^{-1} sec^{-1}). The reactivities of the other alkali ion pairs decrease along the series $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. In dioxane a reverse order is observed.[32] The lithium ion pair is then the least reactive ($k_\pm = 0.9M^{-1}$ sec^{-1}), while the most reactive is the cesium pair.

There is evidence that the ordinary $\sim\!\!S^-,Na^+$ contributes only little to the propagation in tetrahydrofuran. The Arrhenius plot of log $k_\pm$ vs. $1/T$ is shown in Figure 10. Contrary to the conventional behavior of the free $\sim\!\!S^-$ ion or the $\sim\!\!S^-,Cs^+$ ion pair, the "activation energy", $E_\pm$, for $\sim\!\!S^-,Na^+$ propagation is negative. If contact and solvent-separated pairs participate in the reaction, then

$$k_\pm = \gamma k_s + (1 - \gamma)k_c$$

where γ is the fraction of solvent-separated pairs, k_s is their propagation constant, and k_c is the propagation constant of the contact pairs. The equilibrium constant, K_s, of the exothermic conversion of contact pairs

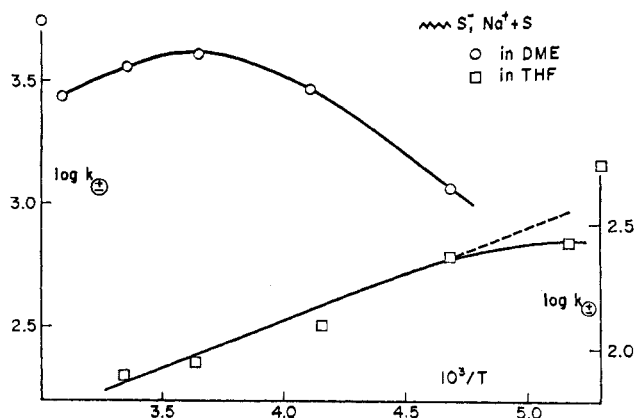(32) D. N. Bhattacharyya, J. Smid, and M. Szwarc, J. Phys. Chem., **69**, 624 (1965).

Figure 10. The Arrhenius line for the propagation constant, $k_\pm$, of the sodium salt of living polystyrene. Upper line: dimethoxy ether; note the maximum in the curve. Lower line: in tetrahydrofuran; note the negative "activation energy."

into solvent-separated is $K_s = \gamma/(1 - \gamma)$ and, hence, for $k_c \ll k_s$
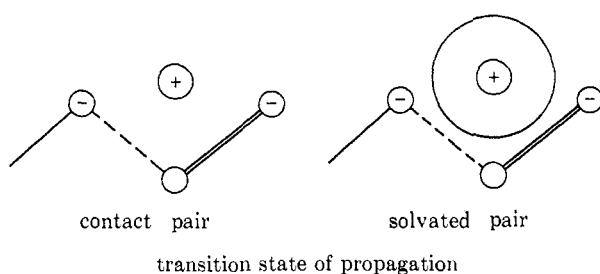
$$E_\pm = E_s + \Delta H_s/(1 + K_s)$$

E_s is the "true" *positive* activation energy of propagation of the solvent-separated pairs and ΔH_s is the heat of solvation. For $K_s \ll 1$, $E_\pm$ is negative when $E_s < -\Delta H_s$. Collating all the available evidence, one concludes that $\Delta H_s = -7.5$ kcal/mol, $E_s = 6$ kcal/mol, and $K_s = 4 \times 10^{-3}$ at 25° and about 0.3 at $-70°$. The propagation constant of the solvent-separated $\sim\!\!S^-,Na^+$ ion pair is, therefore, only slightly lower than that of the $\sim\!\!S^-$ free ion (at 25° $k_s \approx 30,000$ M^{-1} sec^{-1}, while $k_- = 65,000$ M^{-1} sec^{-1}).

Lowering the temperature increases the fraction of the more reactive pairs, and this may more than balance the retarding effect of activation energy and lead to the apparent "negative" activation energy. The gain is voided, however, when the conversion of contact pairs into solvent-separated pairs is high, and then $E_\pm$ becomes positive, although $-\Delta H_s$ is still greater than E_s. This behavior is observed in the polymerization of $\sim\!\!S^-,Na^+$ performed in dimethoxyethane.[33] Due to the bidentate nature of this solvent, the fraction of solvent-separated pairs present in this system is much larger than in tetrahydrofuran. Consequently, the observed $k_\pm$ is substantially higher, e.g., 3600 M^{-1} sec^{-1} at 25° as compared with 80 M^{-1} sec^{-1} found in tetrahydrofuran. Therefore, the relevant Arrhenius line passes through a maximum (see Figure 10) at a reasonably high temperature (actually at 0°). At this temperature $E_s = -\Delta H_s/(1 + K_s)$.

Why is a solvent-separated pair more reactive than a contact pair? A contact pair involves a small, bare cation which becomes partially dissociated in the transition state as shown in the following diagram. This hinders the propagation. The partial dissociation may be unnecessary for the separated pair because the cation is large (due to its solvation).

(33) T. Shimomura, J. Smid, and M. Szwarc, J. Am. Chem. Soc., **89**, 5743 (1967).

contact pair   solvated pair

transition state of propagation

Furthermore, this reaction may involve a "push–pull" mechanism which could make the separated ion pair more reactive even than the free ion. It seems, indeed, that $E_s < E_-$, but the entropy of activation is more negative for the separated ion pair than for the free $\sim\!S^-$ ion. A similar effect was noted for some electron-transfer reactions; the solvent-separated pairs react faster than the free ions, whereas the contact pairs are the least reactive.[26]

The anionic polymerization of sodium polystyryl in tetrahydropyran is affected in a most interesting way by the addition of glyme.[34] The linear dependence of the apparent propagation constant, k_p, on $1/[\text{sodium polystyryl}]^{1/2}$ is changed, as shown in Figure 11. Both the intercepts and slopes increase as the concentration of glyme is raised.

Two additional equilibria are established in the presence of glyme

$$\sim\!S^-,\text{Na}^+ + n\text{ glyme} \rightleftarrows \sim\!S^-(\text{glyme}_n\text{Na}^+)$$

$$\text{Na}^+ + m\text{ glyme} \rightleftarrows \text{Na}^+(\text{glyme})_m$$
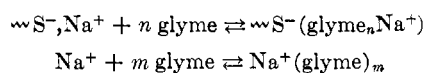
The former yields a new type of ion pair, more reactive than the ordinary one; the latter converts the free Na^+, ions surrounded by solvent molecules into Na^+ ions coordinated with glyme. The higher intercept manifests the formation of the reactive $\sim\!S^-(\text{glyme})_n,\text{Na}^+$ pairs; its increase should be proportional to $[\text{glyme}]^n$. This relation was observed for diglyme and triglyme and n was found to be 1, i.e., only one molecule of either glyme is needed to separate the ions. The steeper slopes are caused by removal of the ordinary Na^+, i.e., $\text{Na}^+ + m$ glyme $\rightleftarrows \text{Na}^+(\text{glyme})_m$. This leads to further dissociation of $\sim\!S^-,\text{Na}^+$ and therefore to a higher proportion of $\sim\!S^-$ ions in the system. Mathematical treatment shows that the increase in

(34) M. Shinohara, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **90**, 2175 (1968).
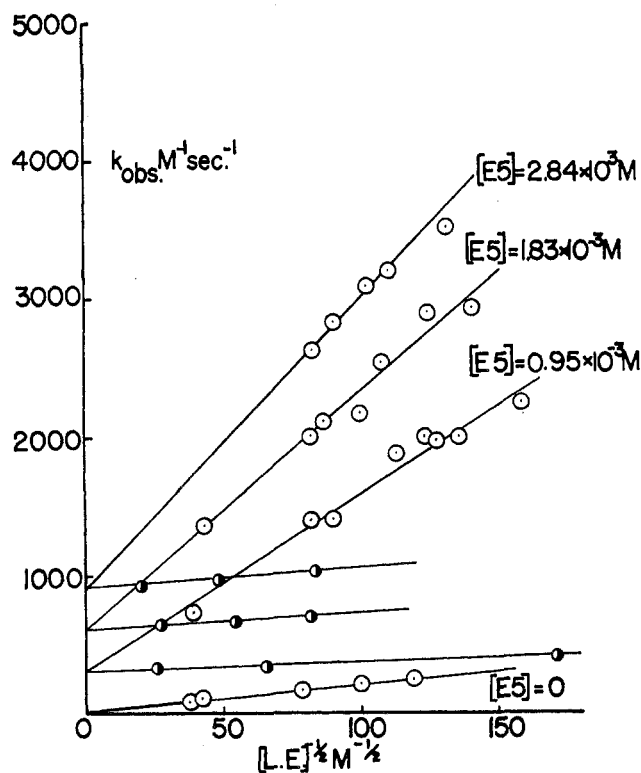

Figure 11. Dependence of the over-all propagation constant of $\sim\!S^-,\text{Na}^+$ in tetrahydropyran on the concentration of living polymers at various constant concentrations of glyme. The half-shaded points represent experiments performed in the presence of sodium tetraphenylboride.

the square of the slope should be proportional to $[\text{glyme}]^m$. The data proved that $m = 2$ for diglyme and 1 for triglyme, i.e., two molecules of diglyme but only one of triglyme are needed to solvate a free Na^+ ion.

In conclusion, I hope that the reality of ion pairs and their existence as independent species endowed with their own individuality are illustrated by the above few examples. More work in this field is needed and further progress is expected in the near future. The esr studies promise to be most valuable in elucidation of many problems encountered in this field.