Radical Anions and Carbanions as Donors in Electron-Transfer Processes

MICHAEL SZWARC

Department of Chemistry, State University College of Forestry at Syracuse University, Syracuse, New York 13210

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Many organic processes result from transfer of electrons (ETP) from one reactant to another. Here we shall discuss only those concerned with radical anions and carbanions acting as electron donors. These ionic species, like others, exist in solution in a variety of forms—as free ions, ion pairs, or still higher aggregates—and their physical and chemical behavior is affected, sometimes profoundly, by their state of aggregation. Moreover, ample physical and chemical evidence demonstrates that the ion pairs may be present in various physically and chemically distinct forms; *e.g.*, the differentiation between tight and loose ion pairs is fully justified and well documented.[1] It is, therefore, my intention to show in this review of various electron-transfer processes how the state of aggregation and the structure of the solvation shell of ionic species affect the rates and the free energies of their reactions. Particularly interesting are those systems in which two or more kinds of distinct ionic species coexist in equilibrium and simultaneously participate in the studied process. The effect of such a coexistence on the electron-transfer equilibria will be considered first, and it will be shown how such studies may lead to the thermodynamic constants determining the equilibria between the various ionic species. Thereafter, we shall deal with the effect of ion pairing on the rate and mechanism of ETP.

Electron-Transfer Equilibria Involving Aromatic Hydrocarbons and Their Radical Anions. Equilibria between aromatic hydrocarbon radical anions and their parent compounds were investigated first by Paul, Lipkin, and Weissman[3] and later by us[4] with the intention of determining the relative electron affinities of the acceptors. The first group described the process as

$$A_1\cdot^- + A_2 \rightleftarrows A_1 + A_2\cdot^- \qquad K_- \quad (1)$$

implying that the transfer involves free anions. However, since tetrahydrofuran was the solvent, Na^+ being the cation, the reported equilibrium constants, $K_\pm$, refer to reactions of ion pairs[4] present in the form, or forms, imposed by the conditions of the experiment, *i.e.*

$$A_1\cdot^-,Na^+ + A_2 \rightleftarrows A_1 + A_2\cdot^-,Na^+ \qquad K_\pm \quad (2)$$

The ratio $K_-/K_\pm$ is equal to $K_{diss,2}/K_{diss,1}$, the last two symbols being the dissociation constants of the respective ion pairs, *e.g.*, $A_1\cdot^-,Na^+ \rightleftarrows A_1\cdot^- + Na^+$. These phenomenological dissociation constants were determined through conductance studies[5] and, hence, the ratios $K_-/K_\pm$ may be calculated. Their values were found to vary from 0.1 to 10.

Reaction 2 does not necessarily represent an elementary process because the ion pairs may exist in more than one form. This is evident from the temperature dependence of the reaction of sodium biphenylide ($B\cdot^-,Na^+$) with naphthalene to form sodium naphthalenide ($N\cdot^-,Na^+$) and biphenyl (eq 3). van't Hoff

$$B\cdot^-,Na^+ + N \rightleftarrows B + N\cdot^-,Na^+ \qquad K_{ap} \quad (3)$$

plots for this equilibrium in three solvents,[6] tetrahydropyran (THP), tetrahydrofuran (THF), and dimethoxyethane (DME), are shown in Figure 1. Although the electron affinity of naphthalene is undoubtedly higher than that of biphenyl, in THF reaction 3 appears to be *endothermic* at lower temperatures. The coexistence of tight and loose ion pairs of $N\cdot^-,Na^+$ and $B\cdot^-,Na^+$ in that solvent accounts for this peculiarity. Indeed, examination of optical spectra of $B\cdot^-,Na^+$ and $N\cdot^-,Na^+$ recorded over a wide temperature range in those three solvents indicates that only tight pairs exist in THP, while in DME only loose pairs are formed[6] at lower temperatures. Moreover, the spectral evidence confirms that both types of pairs are simultaneously present in THF.

The equilibria such as (3a) and (3b) seem to be independent of solvent, at least in first approximation, al-

$$(B\cdot^-,Na^+)_{tight} + N \rightleftarrows B + (N\cdot^-,Na^+)_{tight} \qquad K_{tight} \quad (3a)$$

$$(B\cdot^-,Na^+)_{loose} + N \rightleftarrows B + (N\cdot^-,Na^+)_{loose} \qquad K_{loose} \quad (3b)$$

Michael Szwarc was born in Poland in 1909 and received his undergraduate training at Warsaw Polytechnic College. In 1935 he went to Jerusalem where he taught and was engaged in research at the Hebrew University until 1945. While there, he earned his Ph.D. in organic chemistry. From Israel he went to England, where he received a Ph.D. in physical chemistry in 1947 from the University of Manchester. Two years later he was granted the degree of D.Sc. for his work on dissociation energies of the chemical bond. Dr. Szwarc remained as a lecturer at Manchester until 1952, when he became Professor of Physical and Polymer Chemistry at the State University College of Forestry at Syracuse University, Syracuse, N. Y., and where he is now as the Director of the State University Polymer Research Center. His work during the last ten years has dealt with reactivity of free radicals, cage reactions, anionic polymerization, reactions in aprotic solvents, and the chemistry of radical ions. He is a Fellow of The Royal Society, London.

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(1) The reader interested in this subject may be referred to a short review article by this writer in ref 2a, or to his more extensive monograph, ref 2b.

(2) (a) M. Szwarc, *Accounts Chem. Res.*, **2**, 87 (1969). (b) M. Szwarc, "Carbanions, Living Polymers and Electron-transfer Processes," Interscience, New York, N. Y., 1968, Chapter V.

(3) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, **78**, 116 (1956).

(4) J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).

(5) (a) R. V. Slates and M. Szwarc, *ibid.*, **69**, 4124 (1965); (b) P. Chang, R. V. Slates, and M. Szwarc, *ibid.*, **70**, 3180 (1966).

(6) Y. Karasawa, G. Levin, and M. Szwarc, *Proc. Roy. Soc., Ser. A*, **326**, 53 (1971).

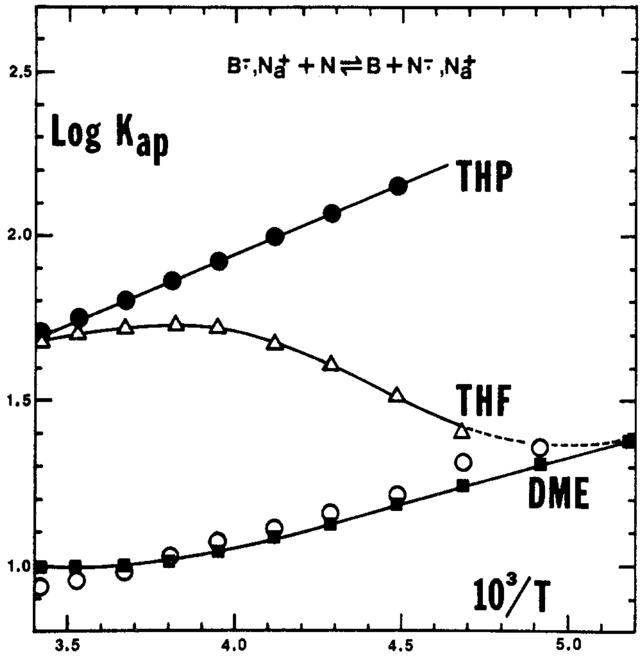

Figure 1. van't Hoff plot, log K_{ap} vs. $1/T$, for the equilibrium $B\cdot^-,Na^+ + N \rightleftarrows N\cdot^-,Na^+ + B$ in THF, THP, and DME. The open circules on DME line give the K_{eq} determined in THP containing 1% tetraglyme. This is sufficient to convert the tight pairs into the loose ones, leaving the nature of solvent virtually unaffected. The results prove, therefore, that the equilibrium involving loose pairs is unaffected by the solvent.

though the solvent's nature strongly affects the equilibria between tight and loose pairs.[2] This assumption is justified elsewhere[6] and, if accepted, it permits us to calculate K_{tight} from the results obtained in THP and K_{loose} by extrapolating the results obtained at lower temperatures in DME.[7] It appears that, for reaction 3, $K_{tight} > K_{loose}$.

Since both types of pairs coexist in THF, the K_{ap} found in this solvent (see Figure 1) represents the ratio

$$\{[(N\cdot^-,Na^+)_{tight}] + [(N\cdot^-,Na^+)_{loose}]\}[B]/\{[(B\cdot^-,Na^+)_{tight}] + [(B\cdot^-,Na^+)_{loose}]\}[N]$$

Simple algebra shows then that

$$K_{ap} = K_{tight}(1 + K_N)/(1 + K_B) = K_{loose}(1 + K_N^{-1})/(1 + K_B^{-1})$$

where K_B and K_N denote the equilibrium constants of the transformations

$$(B\cdot^-,Na^+)_{tight} \rightleftarrows (B\cdot^-,Na^+)_{loose} \qquad K_B$$
$$(N\cdot^-,Na^+)_{tight} \rightleftarrows (N\cdot^-,Na^+)_{loose} \qquad K_N$$

taking place in THF. Moreover, $K_{tight}/K_{loose} = K_B/K_N$, and, thus, merely from the results given in Figure 1, one can calculate K_B and K_N for THF solution. These constants and the related thermodynamic data are compared in Table I with the values obtained by independent spectrophotometric studies.

Table I[a]

Equilibrium of electron-transfer process

$$B\cdot^-,Na^+ + N \rightleftarrows N\cdot^-,Na^+ + B$$

Equilibrium for tight pairs

$\Delta H_{tight} = -2.0$ kcal/mole; $\Delta S_{tight} = +1.0$ eu

Equilibrium for loose pairs

$\Delta H_{loose} = -1.4$ kcal/mole; $\Delta S_{loose} = -1.6$ eu

Equilibrium for $B\cdot^-,Na^+_{tight} \rightleftarrows B\cdot^-,Na^+_{loose}$ (K_B in THF)

$\Delta H_B = -7.9$ kcal/mole; $\Delta S_B = -32$ eu

Equilibrium for $N\cdot^-,Na^+_{tight} \rightleftarrows N\cdot^-,Na^+_{loose}$ (K_N in THF)

$\Delta H_N = -6.9$ kcal/mole; $\Delta S_N = -32$ eu

Equilibrium constant for $B\cdot^-,Na^+_{tight} \rightleftarrows B\cdot^-,Na^+_{loose}$ in THF

Temp, °K	Log K_B Electron-transfer data	Log K_B Spectrophotometric data[5]
282	−0.80	−0.78
262	−0.36	−0.28
253	+0.12	+0.12
223	+0.78	+0.76

Equilibrium constant for $N\cdot^-,Na^+_{tight} \rightleftarrows N\cdot^-,Na^+_{loose}$ in THF

K_N at −70° determined from electron-transfer data	4.8
K_N at −70° determined by esr (Hirota)	4.5

[a] The agreement between K_B and K_N determined by the electron-transfer data and by other independent methods provides further justification for our assumption that the electron-transfer equilibrium for tight or loose pairs is independent of the nature of the solvent, provided one deals with one class of solvents.

Electron Spin Resonance Studies of Kinetics of Electron-Exchange Processes. The application of magnetic resonance techniques to kinetic studies is now well known. The bimolecular rate constants of electron exchange between a paramagnetic radical anion and its parent molecule may be calculated from the shape of the respective esr lines. This technique was utilized first by Weissman and his coworkers[8,9] and thereafter by many other investigators.[10]

An exchange involving free ions is faster than that of tight ion pairs. The rate of the reaction proceeding through free ions is affected by the nature of the solvent because the solvation shell surrounding the original ion must be destroyed in the course of the transfer and a new shell has to be formed around the nonionic acceptor which eventually becomes an ion. The experimental rate constants obtained for the system, naphthalene$\cdot^-$ + naphthalene → exchange, investigated in various solvents are collected in Table II and compared with those calculated by Marcus' treatment[11] involving the parameter λ. The correlation[12] is not perfect; how-

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(7) Tight ion pairs in THP may be converted into loose ones by adding 1% tetraglyme to the solution. The equilibrium constants at these conditions are given in Figure 1 by open circles. The results confirm our assumption that the equilibrium involving loose pairs is independent of the solvent.

(8) R. L. Ward and S. I. Weissman, *J. Amer. Chem. Soc.*, **79**, 2086 (1957).

(9) F. C. Adam and S. I. Weissman, *ibid.*, **80**, 1518 (1958).

(10) Reference 2b, Chapter VI.

(11) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

(12) K. Höfelmann, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, **91**, 4645 (1969).

Table II
Exchange of the Free $N\cdot^-$ Ions with Naphthalene (N)

Solvent	k_{ex} 10^{-8} (at 25°), M^{-1} sec^{-1}	λ, kcal/mole	k_{ex} calcd assuming obsd value for exchange in HMPA	Ref
Isopropyl alcohol	1[a]	16.0	2.5	*b*
HMPA	5	14.5	(5.0)	*c*
THF–DME (1:1)	12	12.5	11.5	*d*
THF	30	12.2	13	*e*

[a] Calculated on the basis of the value for $B\cdot^- + N \rightarrow N\cdot^- + B$ given in footnote *b*. [b] S. Arai and L. M. Dorfman, *Advan. Chem. Ser.*, **No. 82,** 378 (1968). [c] K. Höfelmann, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, **91,** 4645 (1969). [d] N. Hirota, R. Carraway, and W. Schook, *ibid.*, **90,** 3611 (1968). [e] R. Chang and C. S. Johnson, *ibid.*, **88,** 2338 (1966).

ever, a slightly better agreement has been recently reported by Dorfman.[13]

Extensive studies of electron exchanges involving tight and loose ion pairs have been reported by Hirota and his students.[14] Their data, as well as the early findings of Weissman[15] and some of our observations,[12] are collected in Table III. At 25°, tight pairs seem to be 100 times less reactive than the free ions, whereas loose pairs show an intermediate reactivity. A possible explanation of the higher reactivity of loose pairs is discussed in ref 12.

Tight ion pairs may be converted into loose ones by adding to their solution in a poor solvent a small amount of a powerful solvating agent. For example, the addition of tetraglyme, $CH_3(OC_2H_4)_4OCH_3$, to a tetrahydropyran solution of the tight $N\cdot^-,Na^+$ pairs quantitatively converts them to loose ones.[12] Studies of their exchange indicate the presence of two species: one rapidly reacting with naphthalene, $k_{ex} = 25 \times 10^7$ M^{-1} sec^{-1} at 25°, the other being five times less reactive, $k_{ex} = 4.5 \times 10^7$ M^{-1} sec^{-1} (at the same temperature k_{ex} of the tight pair in tetrahydropyran is only 0.2×10^7 M^{-1} sec^{-1}). These results transpire from Figure 2 showing the pertinent esr spectrum recorded at fast exchange limits. The rapid exchange cannot be attributed to the free ions because, as shown by the conductance of the investigated solution, their concentration is too low. It seems, therefore, that two isomeric loose pairs coexist in this system, one being much more reactive than the other.

Electron transfer from an ion pair yields a new ion pair; hence the cation must be transferred in the process. This conclusion was experimentally verified by Adam and Weissman,[16] who investigated the esr spectrum of the sodium salt of benzophenone ketyl in the presence of a large excess of benzophenone. Under such conditions (in the fast exchange limits) the spectrum collapses into four equally intense lines characterizing the sodium nucleus, proving therefore that sodium cations retain their identity in the exchange process. Similar results were reported by us[17] for duroquinone radical anions paired with sodium cations.

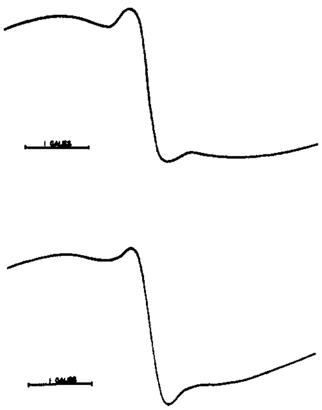

Figure 2. Collapsed esr spectrum of the $N\cdot^-$ (glyme) Na^+ loose pair showing the presence of two species: one exchanging faster, the other slower. Lower curve: computor simulation of the spectrum.

Table III[a]
Rate of Electron Exchange for Tight and Loose Ion Pairs of Naphthalenide Salts with Naphthalene

System	$k_{ex} \times 10^{-7}$ M^{-1} sec^{-1} ~25°	Ref
$N\cdot^-,Na^+$ in THP (tight)	0.2, 0.5	12, 13
$N\cdot^-,Na^+$ in MeTHF (tight)	0.5	13
$N\cdot^-,Na^+$ in Me_2THF (tight)	0.4[b]	14
$N\cdot^-,Na^+$ in THF (tight)	1.2[b]	14
$N\cdot^-,K^+$ in THF (tight)	3.2	14
$N\cdot^-,Cs^+$ in THF (tight)	8.6[b]	14
$N\cdot^-,Li^+$ in THF (loose)	11.5[b]	14
$N\cdot^-,Na^+$ in THF (loose)	20[b]	14
$N\cdot^-,Na^+$ in THF + DME (loose)	15[b]	14
$N\cdot^-,Na^+$ in DME (loose)	15[b]	14
$N\cdot^-,Na^+$ in THP converted into loose pair by adding tetraglyme		
Type I	4.5	12
Type II	25	12

[a] THP, tetrahydropyran; MeTHF, 2-methyltetrahydrofuran; Me_2THF, 2,5-dimethyltetrahydrofuran; DME, dimethoxyethane; tetraglyme, $CH_3(OC_2H_4)_4OCH_3$. [b] These data are obtained from the values given at other temperatures by extrapolation.

Radical anions may also exist as triple ions, *e.g.*, radical anions of duroquinone (DQ) prepared in the presence of sodium tetraphenylboride form $Na^+,DQ\cdot^-,Na^+$ triple ions.[18] We have shown recently[17] that electron transfer from this triple ion to duroquinone proceeds with simultaneous transfer of both cations; the esr spectrum of $Na^+,DQ\cdot^-,Na^+$ triple ions collapses then into seven lines.

Kinetics of Exothermic Electron Transfer. Kinetics of electron transfer from an aromatic hydrocarbon radical anion to another aromatic hydrocarbon of higher electron affinity was studied by Dorfman and his

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(13) J. R. Brandon and L. M. Dorfman, *J. Chem. Phys.*, **53,** 3849 (1970).

(14) N. Hirota, R. Carraway, and W. Shook, *J. Amer. Chem. Soc.*, **90,** 3611 (1968).

(15) P. J. Zandstra and S. I. Weissman, *ibid.*, **84,** 4408 (1962).

(16) F. C. Adam and S. I. Weissman, *ibid.*, **80,** 1518 (1958).

(17) R. F. Adams, T. L. Staples, and M. Szwarc, *Chem. Phys. Lett.*, **5,** 474 (1970).

(18) T. E. Gough and P. R. Hindle, *Can. J. Chem.*, **47,** 1698 (1969); **47,** 3393 (1969).

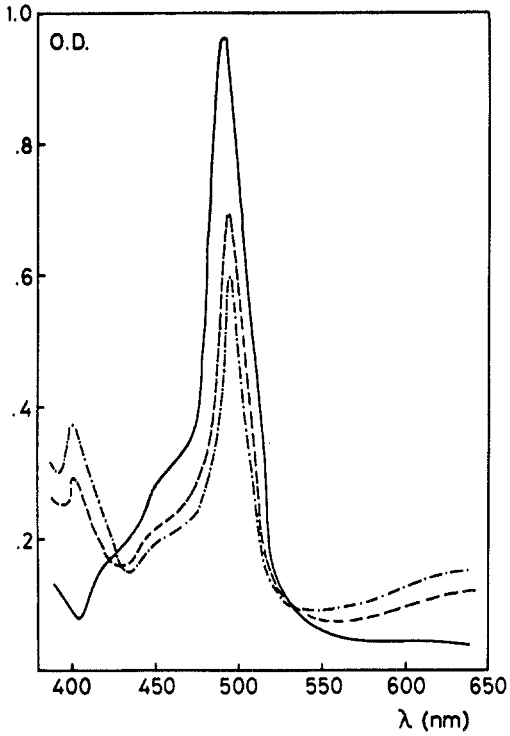

Figure 3. (A, ——) Spectrum of $\pi\cdot^-$ solution containing a 100-fold excess of B before flash and 2 msec after the flash. No peak at 400 nm (λ_{max} of $\mathrm{B}\cdot^-$) is noted. (B, -·- and - -) The spectra taken 50 μsec and 100 μsec, respectively, after the flash. Bleaching of $\pi\cdot^-$ (λ_{max} 490 nm) and appearance of $\mathrm{B}\cdot^-$ (λ_{max} 400 nm) are clearly recognized.

students[13,19] who applied pulse-radiolysis techniques in their work. Similar studies have been reported recently by Fisher, Rämme, Claesson, and Szwarc,[20] who adapted the flash-photolysis technique for their investigations. Their approach is illustrated by the following example.

Consider a solution of sodium pyrenide ($\pi\cdot^-,\mathrm{Na}^+$) containing a 100-fold excess of biphenyl (B). Since the electron affinity of the latter is substantially lower than that of pyrene (π), in spite of the large excess of B no detectable amount of $\mathrm{B}\cdot^-,\mathrm{Na}^+$ is present in such a solution (see Figure 3). The odd electron of $\pi\cdot^-$ may be photoejected by light of proper wavelength (~490 nm, λ_{max} of $\pi\cdot^-$) and hence a flash of actinic light leads to bleaching of the 490-nm band arising from $\pi\cdot^-$ absorption.[20,21] The ejected electrons are captured by biphenyl in a time comparable to the duration of the flash because the concentration of that hydrocarbon is so large. Thus, the absorption at 400 nm (λ_{max} of $\mathrm{B}\cdot^-$) appears simultaneously with the bleaching of the 490-nm band, indicating that $\pi\cdot^- + \mathrm{B}$ was converted into $\pi + \mathrm{B}\cdot^-$ (again see Figure 3). The equilibrium has to be reestablished, and hence reaction 4a or 4b

$$\mathrm{B}\cdot^- + \pi \xrightarrow{k_{4a}} \mathrm{B} + \pi\cdot^- \tag{4a}$$

$$\mathrm{B}\cdot^-,\mathrm{Na}^+ + \pi \xrightarrow{k_{4b}} \mathrm{B} + \pi\cdot^-,\mathrm{Na}^+ \tag{4b}$$

ensues, its progress being monitored by the optical density either at 400 nm or 490 nm. In extremely dilute THF solutions of $\pi\cdot^-,\mathrm{Na}^+$, *viz.*, $2\text{–}4 \times 10^{-7}\,M$, the dissociation of the ion pairs into free ions is virtually quantitative and, therefore, under such conditions reaction 4a is observed. On the other hand, the photolysis of solutions containing excess of sodium tetraphenylboride permits us to determine k_{4b}.

The results show again that free ions react more readily than ion pairs, although the ratio k_{4a}/k_{4b} is smaller than the corresponding ratio of a thermoneutral exchange reaction.[22]

Electron Capture Processes and the Collapse of $\mathrm{e}^-,\mathrm{Na}^+$ Pair into Na Atom. Flash photolysis of the pyrenide ($\pi\cdot^-$) solution performed in the absence of biphenyl leads to the formation of a transient (λ_{max} ~800 nm) which was identified as the solvated electron–sodium cation pair ($\mathrm{e}^-,\mathrm{Na}^+$).[21,23] Both solvated electrons (e^-) and the pairs ($\mathrm{e}^-,\mathrm{Na}^+$) are produced in dilute solution, and from their ratio it was possible to estimate the dissociation constant of the latter,[20] *viz.*

$$\mathrm{e}^-,\mathrm{Na}^+ \rightleftharpoons \mathrm{e}^- + \mathrm{Na}^+$$

$$K_{diss} \sim 0.5 \times 10^{-7}\,M \text{ in THF at } 25°$$

Subsequently, reactions 5a and 5b ensue, and the kinetic

$$\mathrm{e}^- + \pi \longrightarrow \pi\cdot^- \tag{5a}$$

$$k_{5a} = 10 \times 10^{10}\,M^{-1}\,\mathrm{sec}^{-1}$$

$$\mathrm{e}^-,\mathrm{Na}^+ + \pi \longrightarrow \pi\cdot^-,\mathrm{Na}^+ \tag{5b}$$

$$k_{5b} = 1.4 \times 10^{10}\,M^{-1}\,\mathrm{sec}^{-1}$$

studies provided the respective electron-capture rate constants,[18] k_{5a} being again higher than k_{5b}.

The rate of reappearance of $\pi\cdot^-$ has been found to be much slower than the rate of disappearance of the transient. Nevertheless, *all* the $\pi\cdot^-$ initially present in the solution is re-formed at the end of the reaction. Hence, some additional process adds to the faster disappearance of the transient than the reappearance of $\pi\cdot^-$. This process was shown to be unimolecular and it has to yield a species which eventually reacts with pyrene and forms $\pi\cdot^-$. It has been concluded, therefore, that a collapse of the $\mathrm{e}^-,\mathrm{Na}^+$ pair into Na atoms is responsible for the observed phenomena,[20] its unimolecular rate constant being ~10^4 sec^{-1} in THF and somewhat higher in THP. A faster collapse of the pair in solvents of lower solvating power is indeed expected.

Electron Transfers Leading to the Formation of Dianions. Disproportionation of radical anions exemplifies an electron-transfer reaction leading to the formation of dianions, *viz.*, $2\mathrm{A}\cdot^- \rightleftharpoons \mathrm{A}^{2-} + \mathrm{A}$. The equilibrium constant of such a process is greatly affected

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(19) S. Arai, D. A. Grev, and L. M. Dorfman, *J. Chem. Phys.*, **46**, 2572 (1967); see also L. M. Dorfman, *Accounts Chem. Res.*, **3**, 224 (1970).

(20) M. Fisher, G. Rämme, S. Claesson, and M. Szwarc, *Chem. Phys. Lett.*, **9**, 306, 309 (1971); *Proc. Roy. Soc., Ser. A*, **327**, 467, 481 (1972).

(21) (a) G. J. Hoijtink and P. J. Zandstra, *Mol. Phys.*, **3**, 371 (1963); (b) J. D. W. van Voorst and G. J. Hoijtink, *J. Chem. Phys.*, **42**, 3995 (1965); **45**, 3918 (1966); (c) J. Eloranta and H. Linschitz, *ibid.*, **38**, 2214 (1963); (d) L. J. Giling, J. G. Kloosterboer, R. P. H. Rettschnick, and J. D. W. van Voorst, *Chem. Phys. Lett.*, **8**, 457 (1971).

(22) R. Chang and C. S. Johnson, *J. Amer. Chem. Soc.*, **88**, 2338 (1966).

(23) J. G. Kloosterboer, L. J. Giling, R. P. H. Rettschnick, and J. D. W. van Voorst, *Chem. Phys. Lett.*, **8**, 462 (1971).

by the state of aggregation and solvation of the reagents.[24] Studies of disproportionation of radical anions of tetraphenylethylene ($T\cdot^-$), reported from this laboratory,[25,26] showed that the disproportionation is unfavorable for the free $T\cdot^-$ ions in hexamethylphosphoric triamide (HMPA), *i.e.*, for reaction 6a, but

$$2T\cdot^- \rightleftarrows T^{2-} + T \qquad (6a)$$

$k_{6a} \sim 10^{-4}$ in HMPA at 20°

as the degree of aggregation of the ionic species increases the equilibrium shifts to the right, as in reactions 6b and 6c. These disproportionations are *endothermic,*

$$T\cdot^- + T\cdot^-,Na^+ \rightleftarrows T^{2-},Na^+ + T \qquad (6b)$$

$k_{6b} = 3.3$ in THF at 20°

$$2T\cdot^-,Na^+ \rightleftarrows T^{2-},2Na^+ + T \qquad (6c)$$

$k_{6c} = 400$ in THF at 20°

viz., $\Delta H_{6b} = 13$ kcal/mole and $\Delta H_{6c} = 19$ kcal/mole, and proeeed with an *increase* of the entropy of the system, *viz.*, ΔS_{6b} and ΔS_{6c} are large and positive. Hence, the driving force for disproportionation arises from entropy increase, caused by the desolvation of the products, and not from a decrease in the energy of the system. Conductance studies[25] demonstrate that disproportionation converts the loose, well solvated $T\cdot^-$,Na^+ pairs into tight $T^{2-},2Na^+$ aggregates with simultaneous release of the solvent molecules from the solvation shells.

The effect of pairing and aggregation is more pronounced in disproportionation than in other electron-transfer processes because the conversion of mononegative ions into dinegative ions is greatly facilitated by pairing of the latter with cations.

The kinetics of this disproportionation also are greatly affected by the state of aggregation of the reagents. This is shown in our recent, yet unpublished studies utilizing flash-photolytic technique. Under our experimental conditions most of the radical ions were dissociated into free ions; $T\cdot^-,Na^+$ pairs formed only 2–5% of the $T\cdot^-$ ions. Nevertheless, the disproportionation of $T\cdot^-$ ions (reaction 6a) was too slow to contribute to the observed process ($k_{6a} < 10^3\ M^{-1}\ \mathrm{sec}^{-1}$), presumably because of the repulsion experienced by the negative ions. The rate constant of reaction 6b was determined to be $7 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$ (at ambient temperature in THF) and only an upper limit $k_{6c} < 4 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$ could be deduced for the disproportionation of the two $T\cdot^-,Na^+$.

An interesting example of an electron transfer leading to formation of dianions has been reported by Dadley and Evans.[27] A slow reaction ensues on mixing THF solutions of diphenylacetylene radical anions ($DPA\cdot^-$,Na^+) and sodium salts of phenanthrenide or naphthalenide ($N\cdot^-,Na^+$) anions. The reaction was found to be first order with respect to each reagent, both being consumed in 1:1 stoichiometric ratio, suggesting that a simple electron-transfer process (eq 7) takes place.

$$DPA\cdot^-,Na^+ + N\cdot^-,Na^+ \xrightarrow{k_7} DPA^{2-},2Na^+ + N \qquad (7)$$

However, since we have found that $DPA^{2-},2Na^+$ is rapidly protonated by THF[28] at temperatures higher than −60°, *viz.*

$$DPA^{2-},2Na^+ + THF \xrightarrow{k_8} PhCH{=}\bar{C}Ph,Na^+ + \text{products of THF deprotonation} \qquad (8)$$

we decided to reinvestigate that process.[29] The claims of Dadley and Evans were confirmed, but in addition the reaction was shown to be retarded by naphthalene,[29] *i.e.*

$$-d[DPA\cdot^-,Na^+]/dt = \text{constant} \times [DPA\cdot^-,Na^+][N\cdot^-,Na^+]/[N] \qquad (9)$$

Hence, two steps are involved: (a) a rapidly established equilibrium maintaining a *minute* equilibrium concentration of $DPA^{2-},2Na^+$, and (b) the rate determining, pseudounimolecular protonation (eq 8). The rate constant derived from the kinetic studies gives, therefore, not k_7 but the product k_8K_7, where K_7 denotes the equilibrium constants of reaction 7.

Electron transfer from sodium biphenylide to methylphenylacetylene (MPA) leads also to dianion formation. This reaction, studied at room temperature by a stop-flow technique,[30] was shown to be second order in biphenylide provided MPA and biphenyl were in excess of $B\cdot^-,Na^+$. However, the second-order rate constants derived from the individual runs were found to be proportional to $\{[MPA]/[B]\}^2$, as demonstrated by Figures 4 and 5. Hence, the kinetics of the overall process is given by

$$-d[B\cdot^-,Na^+]/dt = \text{constant} \times \{[B\cdot^-,Na^+][MPA]/[B]\}^2$$

The products have been identified as $Ph\bar{C}{=}C{=}CH_2$,Na^+ and $Ph\bar{C}{=}CHCH_3,Na^+$ because their protonation yielded phenylallene and β-methylstyrene.

Two mechanisms may account for these findings. A minute equilibrium concentration of $MPA\cdot^-,Na^+$ radical anions is maintained by a rapidly established equilibrium (eq 10), and the rate determining H-atom

$$MPA + B\cdot^-,Na^+ \rightleftarrows MPA\cdot^-,Na^+ + B \qquad K_{10} \quad (10)$$

transfer (eq 11) leads to the final products. In terms

$$2PhC{\equiv}CMe\cdot^-,Na^+ \xrightarrow{k_{11}} Ph\bar{C}{=}C{=}CH_2,Na^+ + Ph\bar{C}{=}CHCH_3,Na^+ \qquad (11)$$

of this mechanism the observed rate constant is given by $k_{11}K_{10}^2$.

Alternatively, one may suggest a further electron-

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(24) (a) J. F. Garst and R. S. Cole, *J. Amer. Chem. Soc.*, **84**, 4352 (1962); (b) J. F. Garst, E. R. Zabolotny, and R. S. Cole, *ibid.*, **86**, 2257 (1964); (c) J. F. Garst and E. R. Zabolotny, *ibid.*, **87**, 495 (1965).

(25) R. C. Roberts and M. Szwarc, *J. Amer. Chem. Soc.*, **87**, 5542 (1965).

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

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(28) G. Levin, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, **92**, 2268 (1970).

(29) G. Levin, J. Jagur-Grodzinski, and M. Szwarc, *Trans. Faraday Soc.*, **67**, 768 (1971).

(30) G. Levin and M. Szwarc, *J. Chem. Soc.*, *Chem. Commun.*, in press.

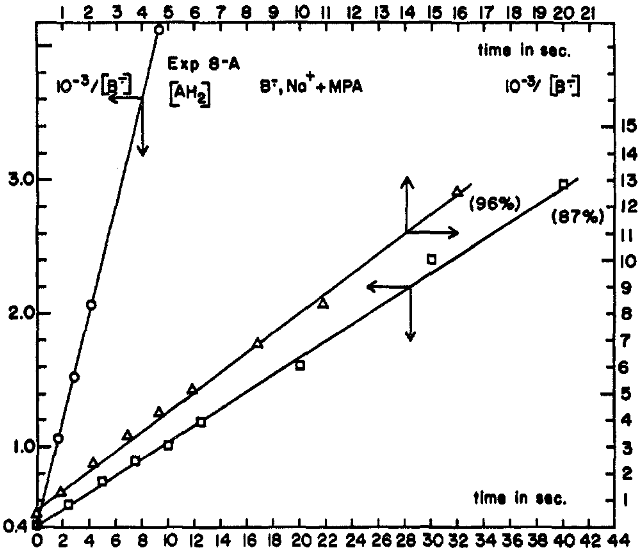

Figure 4. Typical *second-order* plots $1/[B\cdot^-,Na^+]$ *vs.* time for the reaction MPA + $B\cdot^-,Na^+$. Experiment 8-A (⊙) was performed in the presence of dihydroanthracene (AH_2) but otherwise under conditions identical with those prevailing in (□). Note the second-order character of expt 8-A and its faster rate. The arrows point to the pertinent scales of time and $10^{-3}/[B^-]$.

transfer equilibrium to follow equilibrium 10, namely, eq 12. Equilibrium 12 in conjunction with (10) maintains an equilibrium concentration of the $MPA^{2-},2Na^+$ dianions, the latter being present perhaps at even lower concentration than the radical anions. The reaction is driven then by the rate-determining proton transfer from the unreacted MPA to the powerful $MPA^{2-},2Na^+$ base, *viz.*, eq 13. This mechanism also accounts for the observed products and the kinetics, and in its terms the kinetically determined rate constant is $k_{13}K_{10}K_{12}$.

$$MPA\cdot^-,Na^+ + B\cdot^-,Na^+ \rightleftarrows MPA^{2-},2Na^+ + B \qquad K_{12} \qquad (12)$$

$$MPA^{2-},2Na^+ + MPA \xrightarrow{k_{13}} Ph\bar{C}{=}CHCH_3,Na^+ + Ph\bar{C}{=}C{=}CH_2,Na^+ \qquad (13)$$

To discriminate between the two mechanisms, we investigated the interaction of MPA with $B\cdot^-,Na^+$ in the presence of an excess of dihydroanthracene (DHA). This hydrocarbon acts as an acid, stronger than MPA but too weak to protonate $B\cdot^-,Na^+$ in a time needed for completion of the investigated process (less than 2 min). As shown in Figure 4, the addition of DHA greatly accelerated the rate of the reaction, which nevertheless remained *second order* in $B\cdot^-,Na^+$. Such an effect is predicted by the second mechanism, but not by the first; it implies therefore that the dianions are again the intermediates in the overall process.

Another example of a reaction involving dianion intermediates was reported by Lagendijk and Szwarc.[31] Electron transfer from biphenylide ($B\cdot^-$) to 1,2-di-α-naphthylethane (NCH_2CH_2N) produces the radical anions of the latter hydrocarbon ($NCH_2CH_2N\cdot^-$).

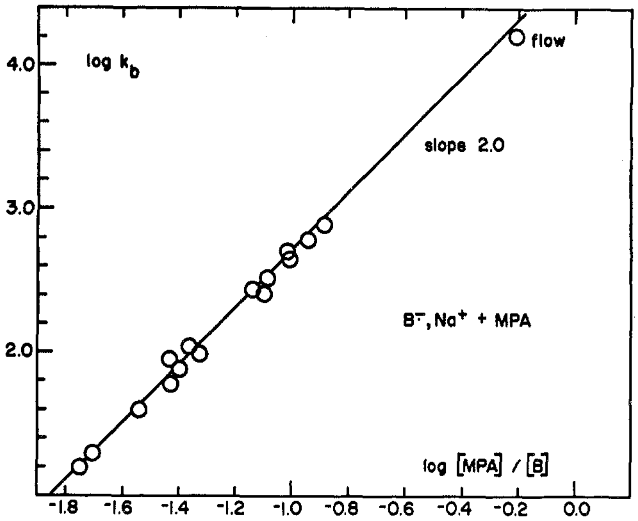

Figure 5. Plot of the log of the apparent bimolecular rate constant, k_b, derived from plots such as shown in Figure 4, *vs.* log {[MPA]/[B]}. The line has slope 2.0.

Although the free radical ions formed in hexamethylphosphoric triamide (HMPA) seem to be stable, the ion pairs decompose, yielding a salt of the NCH_2^- carbanion. Kinetics of this decomposition showed its rate to be second order in radical anions and inversely proportional to the concentration of the unconverted hydrocarbon; *i.e.*, rate $\sim [NCH_2CH_2N\cdot^-,Alk^+]^2/[NCH_2CH_2N]$. Hence, the reaction again proceeds through the dianion, *viz.*, eq 14, followed by the rate-determining fission of the C–C bond of the dianion which takes place simultaneously with the formation of carbanions, *i.e.*, eq 15. The overall rate constant is given by $k_{15}K_{14}$ and its value is greatly affected by the nature of the counterion and the solvent. This is to be expected, because the formation of the dianion is favored by its pairing with cations and in its absence equilibrium (eq 14) is shifted far to the left. Thus, the stability of the free $NCH_2CH_2N\cdot^-$ radical ion in HMPA is accounted for. At present we do not know how the nature of the ion pairs affects the rate of dissociation 15.

$$2NCH_2CH_2N\cdot^-,Alk^+ \rightleftarrows Alk^+,{}^-\cdot NCH_2CH_2N\cdot^-,Alk^+ + NCH_2CH_2N \qquad K_{14} \qquad (14)$$

$$Alk^+,{}^-\cdot NCH_2CH_2N\cdot^-,Alk^+ \xrightarrow{k_{15}} 2NCH_2^-,Alk^+ \qquad (15)$$

Role of Dianions in Some Protonation Reactions. We have found that the protonation of some radical anions proceeds through dianions.[29,32] The question arises why the final products are not formed directly, *e.g.*, reactions 7 and 8 could be substituted through the sequence

$$DPA\cdot^-,Na^+ + \text{proton donor} \longrightarrow PhCH{=}\dot{C}Ph + \ldots.$$

followed by the fast electron transfer

$$PhCH{=}\dot{C}Ph + DPA\cdot^-,Na^+ \text{ (or } N\cdot^-,Na^+) \longrightarrow PhCH{=}\bar{C}Ph,Na^+ + DPA \text{ (or N)}$$

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[31] A. Lagendijk and M. Szwarc, *J. Amer. Chem. Soc.*, **93**, 5359 (1971).

[32] G. Levin, C. Sutphen, and M. Szwarc, *J. Amer. Chem. Soc.*, **94**, 2652 (1972).

The protonation of a radical anion—a relatively weak base—by a *weak* acid seems to require a prohibitively high activation energy, while the protonation of a dianion—a powerful base—is facile. Thus, in spite of their low concentration dianions provide an easier route to the products than radical anions.

This conclusion may be valid for other systems. For example, our recent studies of protonation of perylene radical anions ($\text{Pe}\cdot^-,\text{Na}^+$) by methyl, ethyl, isopropyl, and *tert*-butyl alcohols in THF showed that the reaction is second order in radical anions and it is retarded by perylene.[32] Obviously, this protonation again involves dianions, *viz.*

$$2\text{Pe}\cdot^-,\text{Na}^+ \rightleftarrows \text{Pe}^{2-},2\text{Na}^+ + \text{Pe}$$

$$\text{Pe}^{2-},2\text{Na}^+ + \text{ROH} \longrightarrow \text{protonation products}$$

Protonation of anthracene radical anions by alcohols has been reported recently by Minnic hand Dye,[33] who found the reaction to be second order in radical anions. They concluded that dimers, *e.g.*, $(\text{A}\cdot^-,\text{K}^+)_2$, are protonated faster than the nonassociated radical anions, an unlikely event. It seems to us that the dianion, $\text{A}^{2-},2\text{Na}^+$, is again the intermediate, and indeed the effect of anthracene addition recently investigated by us confirms this conclusion.

The dianions may be protonated even by diethyl ether. For example, Dowd[34] showed that on contact with metallic sodium, tetraphenylallene in diethyl ether yields $\text{Ph}_2\text{C}{=}\text{CH}\bar{\text{C}}\text{Ph}_2,\text{Na}^+$. Apparently, the dianions are formed first and these are protonated by the ether.

Electron Transfer from Carbanions to Aromatic Acceptors. A carbanion may be oxidized to the corresponding radical through transfer of its electron to a suitable acceptor. The first example of such a reaction was reported by Schlenk[35] at the beginning of this century, *viz.*, $\text{Ph}_3\text{C}^- + \text{A} \rightarrow \text{Ph}_3\text{C}\cdot + \text{A}\cdot^-$. We have been interested in similar reactions involving dicarbanions of the dimeric 1,1-diphenylethylene. Radical anions of 1,1-diphenylethylene ($\text{D}\cdot^-,\text{Na}^+$) rapidly dimerize,[36] yielding dimeric dicarbanions $\text{Na}^+,\bar{\text{C}}(\text{Ph})_2\text{CH}_2\text{CH}_2\bar{\text{C}}(\text{Ph})_2,\text{Na}^+ = \text{Na}^+,{}^-\text{DD}^-,\text{Na}^+$. Powerful electron acceptors such as perylene (Pe) oxidize $\text{Na}^+,{}^-\text{DD}^-,\text{Na}^+$, and probably a two-electron transfer takes place causing dissociation of the dimer, *viz.*

$$\text{Na}^+,{}^-\text{DD}^-,\text{Na}^+ + \text{Pe} \longrightarrow 2\text{D} + \text{Pe}^{2-},2\text{Na}^+$$

although two consecutive electron transfers to two Pe cannot be ruled out. However, less potent acceptors such as anthracene (A), 9,10-dimethylanthracene (DMA), or pyrene (π) remove only one electron from the dicarbanion[35] and subsequently the equilibrium exemplified by eq 16 is established.

$$\text{Na}^+,{}^-\text{DD}^-,\text{Na}^+ + \text{A} \rightleftarrows \text{Na}^+,{}^-\text{DD}\cdot + \text{A}\cdot^-,\text{Na}^+ \qquad K_{16,\text{A}} \qquad (16)$$

Apparently $\text{Na}^+,{}^-\text{DD}\cdot$ resists oxidation by the less powerful acceptors like anthracene but undergoes dissociation, *viz.*, eq 17,

$$\text{Na}^+,{}^-\text{DD}\cdot \xrightarrow{k_{17}} \text{D}\cdot^-,\text{Na}^+ + \text{D} \qquad (17)$$

which is followed by a rapid electron transfer, *e.g.*, $\text{D}\cdot^-,\text{Na}^+ + \text{A} \rightarrow \text{A}\cdot^-,\text{Na}^+ + \text{D}$. Thus, ${}^-\text{DD}^-$ (cations are omitted for the sake of brevity) eventually decomposes into 2D, reaction 17 being the rate-determining step. This peculiar mechanism implies that the decomposition is autoinhibited and retarded by the initially added $\text{A}\cdot^-,\text{Na}^+$, both conclusions verified by experiments.[37] The overall rate constant is given by $k_{17}K_{16}$. Kinetic studies of two systems, say ${}^-\text{DD}^- + \text{A}$ and ${}^-\text{DD}^- + \pi$, provide then two values, $k_{17}K_{16,\text{A}}$ and $k_{17}K_{16,\pi}$, whose ratio is $K_{16,\text{A}}/K_{16,\pi}$ because k_{17} is common for both. However, $K_{16,\text{A}}/K_{16,\pi}$ is equal to the equilibrium constant of $\pi\cdot^-,\text{Na}^+ + \text{A} \rightleftarrows \pi + \text{A}^-,\text{Na}^+$, and this conclusion again was verified experimentally.[38]

Does an electron transfer require the formation of an adduct which mediates the reaction?[39] Adducts were not observed in electron transfers from the ${}^-\text{DD}^-$ salts to aromatic acceptors, although closely similar reactions, involving dimeric dicarbanions of α-methylstyrene, ${}^-\alpha\alpha^- = \bar{\text{C}}(\text{Ph})(\text{CH}_3)\text{CH}_2\text{CH}_2\bar{\text{C}}(\text{Ph})(\text{CH}_3)$, revealed the formation of such adducts. A bimolecular reaction of anthracene with $\text{K}^+,{}^-\alpha\alpha^-,\text{K}^+$ is fast ($k \sim 5000\ M^{-1}\ \text{sec}^{-1}$) and forms an adduct absorbing at 451 mm.[40] A covalent bond is formed then between the terminal C atom of the dimer and C-9 of anthracene, the negative charge being transfered to C-10, the resulting structure being abbreviated by ${}^-\alpha\alpha\text{–A}^-$. The adduct decomposes within 1 or 2 min by fission of the α–A bond, yielding the salt of $\text{A}\cdot^-$ as the final product. Kinetics of this decomposition implies the following mechanism.[41] A rapidly established equilibrium maintains a minute concentration of dimeric radical carbanions, ${}^-\alpha\alpha\cdot$ (eq 18), which decompose in a rate-determining step (eq 19) giving α-methylstyrene and

$$\text{K}^+,{}^-\alpha\alpha\text{–A}^-,\text{K}^+ \rightleftarrows \text{K}^+,{}^-\alpha\alpha\cdot + \text{A}\cdot^-,\text{K}^+ \qquad K_{18} \qquad (18)$$

$$\text{K}^+,{}^-\alpha\alpha\cdot \xrightarrow{k_{19}} \alpha\cdot^-,\text{K}^+ + \alpha \qquad (19)$$

α-methylstyrene radical anions, $\alpha\cdot^-$. The latter rapidly transfers its electron to anthracene. According to this mechanism the reaction should be autoinhibited and retarded by the initially added $\text{A}\cdot^-,\text{K}^+$. This behavior was indeed observed.

The above mechanism accounts for the behavior of the system provided ${}^-\alpha\alpha^-$ is in a large excess. How-

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(33) E. R. Minnich and J. L. Dye, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971.

(34) P. Dowd, *J. Chem. Soc.*, 568 (1965).

(35) W. Schlenk and R. Ochs, *Ber.*, **49**, 608 (1916).

(36) M. Matsuda, J. Jagur-Grodzinski, and M. Szwarc, *Proc. Roy. Soc., Ser. A*, **288**, 212 (1965).

(37) (a) J. Jagur-Grodzinski, M. Levy, M. Feld, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 2168 (1962); (b) J. Jagur-Grodzinski and M. Szwarc, *Proc. Roy. Soc., Ser. A*, **288**, 224 (1965).

(38) D. Gill, J. Jagur-Grodzinski, and M. Szwarc, *Trans. Faraday Soc.*, **60**, 1424 (1964).

(39) The reacting partners have to "collide" in order to react (the collision cross section need not be specified in our argument). The collision adduct will be treated as a chemically distinct species only if its lifetime is much longer than the usual encounter time of two molecules in a liquid ($\sim 10^{-10}$ sec).

(40) R. Lipman, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, **87**, 3005 (1965).

(41) J. Jagur-Grodzinski and M. Szwarc, *Trans. Faraday Soc.*, **59**, 2305 (1963).

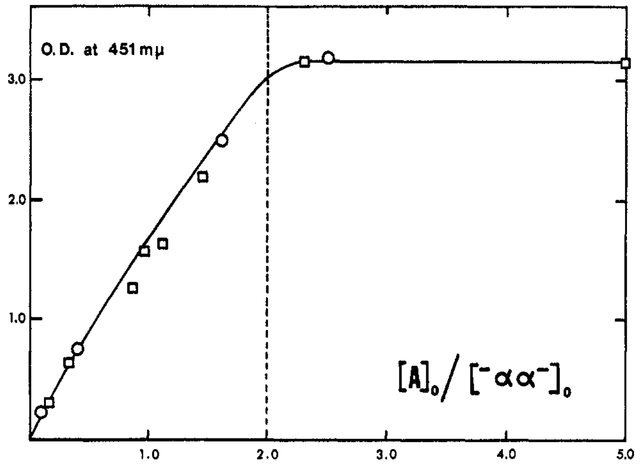

Figure 6. Optical density at 451 nm (λ_{max} of the adduct between $^-\alpha\alpha^-$ and anthracene) at $[^-\alpha\alpha^-]_0$ = constant and variable $[A]_0$ plotted as the function of $[A]_0/[^-\alpha\alpha^-]_0$; observed in a flow system about 0.2 sec after mixing the reagents (solvent THF, 25°, counterion K^+).

ever, strange results are obtained when the concentration of $^-\alpha\alpha^-$ is kept constant while the concentration of anthracene is varied.[41] In each experiment the conversion of anthracene to the adduct is completed in a fraction of a second and, as shown in Figure 6, all the added anthracene reacts, provided the molar ratio $[A]_0/[^-\alpha\alpha^-]_0$ does not exceed 2. This is plausible; the fast anthracene addition, (20), proceeds further

$$K^+,{}^-\alpha\alpha^-,K^+ + A \longrightarrow K^+,{}^-\alpha\alpha\text{-}A^-,K^+ \tag{20}$$

equally fast,[37] *viz.*

$$K^+,{}^-A\text{-}\alpha\alpha^-,K^+ + A \longrightarrow K^+,{}^-A\text{-}\alpha\alpha\text{-}A^-,K^+ \tag{21}$$

and eventually 2A may react with each $^-\alpha\alpha^-$.

For a constant $[^-\alpha\alpha^-]_0$ and variable $[A]_0$, one could expect the *initial* rate of adduct decomposition, R_0, to increase with $[A]_0$ provided $[A]_0/[^-\alpha\alpha^-]_0 \leq 2$. This, however, is not the case. As shown in Figure 7, R_0 first increases, reaches a maximum for $[A]_0/[^-\alpha\alpha^-]_0 = 1$, and then decreases. This peculiarity is explicable if the decomposition of $K^+,{}^-\alpha\alpha\cdot$ (reaction 19) is relatively rapid while the dissociation of $K^+,{}^-A\text{-}\alpha\alpha\cdot$ is very slow. The formation of *two* C=C bonds enhances reaction 19, whereas only one C=C bond is gained in the dissociation

$$K^+,{}^-A\text{-}\alpha\alpha\cdot \longrightarrow K^+,{}^-A\text{-}\alpha\cdot + \alpha$$

making it substantially slower than (19). Denoting the ratio $[A]_0/[^-\alpha\alpha^-]_0$ by $2p$, one finds the mole fraction of the initially formed $^-\alpha\alpha\text{-}A^-$ to be $2p(1 - p)$ provided the reactivity of each $^-\alpha\alpha^-$ end is not affected by the fate of the other. Thus, the observed rate should be proportional to $p(1 - p)$, accounting for the results shown in Figure 7.

The same basic behavior was observed in reactions of $^-\alpha\alpha^-$ with pyrene and benzpyrene.[42] A fully documented account of oxidation of $^-DD^-$ and $^-\alpha\alpha^-$ by aromatic hydrocarbons has been published recently.[43]

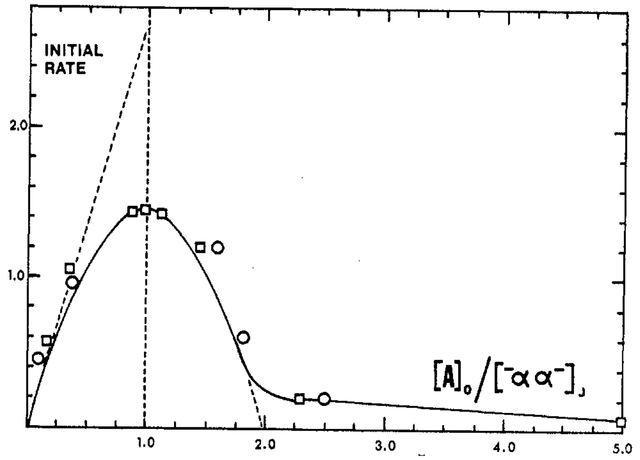

Figure 7. The rate of the initial formation of $A\cdot^-$; $R_0 = (d[A\cdot^-]/dt)_0$ plotted *vs.* $[A]_0/[^-\alpha\alpha^-]_0$ (25°, solvent THF). Note the theoretical curve (parabola) and R_0 = max at $[A]_0/[^-\alpha\alpha^-]_0 = 1$.

Interaggregate Electron Transfer. The soluble sodium salt of the dianions of diphenylacetylene ($DPA^{2-},2Na^+$) is stable in THF at −80°.[22] On addition of methanol the resulting protonation yields an equimolar mixture of dibenzyl- and diphenylacetylene and a small amount of *trans*-stilbene. This surprising result could be explained by an extremely fast electron transfer from the unprotonated $DPA^{2-},2Na^+$ to the formed stilbene—a transfer which should successfully compete with the protonation by methanol. To test this suggestion, a solution of methanol and *stilbene* was added to the $DPA^{2-},2NA^+$ solution. In view of the large excess of stilbene one should expect in such an experiment a quantitative conversion of $DPA^{2-},2Na^+$ into DPA and the formation of an equivalent amount of dibenzyl. However, no visible effect of the added stilbene was noted; the resulting products were still composed of equimolar mixtures of DPA and dibenzyl, proving that stilbene does not compete efficiently with methanol for $DPA^{2-},2Na^+$, after all. We can offer only one explanation of these findings. Apparently $DPA^{2-},2Na^+$ exists under conditions of these experiments in dimeric, or more likely polymeric form, *i.e.*, $(DPA^{2-},2Na^+)_n$. Protonation of $DPA^{2-},2Na^+$ imbedded in the aggregate yields stilbene which undergoes an *intra-aggregate* electron transfer before it has the chance to diffuse out. The intraaggregate electron transfers may efficiently compete with *inter*molecular protonation, although the intermolecular transfer to the added stilbene is relatively inefficient.

This example demonstrates again how the course of an electron-transfer reaction is affected by the state of aggregation of the ionic donor.

Financial support of these studies by the National Science Foundation is gratefully acknowledged. Also, I am indebted to my coworkers and students who performed the work described in this paper, especially to Dr. J. Jagur-Grodzinski and Dr. G. Levin.

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[42] C. S. Chadha, J. Jagur-Grodzinski, and M. Szwarc, *Trans. Faraday Soc.*, **63**, 2994 (1967).

[43] J. Jagur-Grodzinski and M. Szwarc, *J. Amer. Chem. Soc.*, **91**, 7594 (1969).