Electron and Proton Transfer Reactions of Aromatic Molecule Ions in Solution

LEON M. DORFMAN
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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The chemical behavior of organic molecule ions and radical ions as reactive intermediates in solution is a fascinating subject with relevance to the study of organic reaction mechanisms, solution kinetics, radiation chemistry, and radiation biology. The electronic structure of aromatic radical anions and cations has been extensively studied by optical absorption spectroscopy and electron spin resonance spectroscopy. Electrochemical methods have been useful in elucidating many of the chemical equilibria in which they are involved. For investigation of the kinetic behavior of aromatic radical ions in solution, perhaps the most effective method has been the fast reaction technique of pulse radiolysis[1–3] with direct time-resolved observation.

In pulse radiolysis, ionization is produced by a burst of high-energy electrons from an accelerator. In systems of aromatic hydrocarbons in organic solvents, it has been found that radiolysis will yield either the aromatic anion or the cation, depending on the solvent chosen. A great many kinetic studies of aromatic radical anions, and more recently of cations, have been so carried out, free from the complexities of alkali metal ion catalysis or ion pairing which occur in other systems. By working at low concentrations of all reactive species formed, it is relatively straightforward, in most systems, to isolate the individual elementary reaction under investigation and to avoid involvement of extraneous species.

Quantitative rate data have been obtained[4,5] for ion formation (by electron attachment in the case of the radical anion and by charge transfer in the case of the cation) and for ion decay by reaction with the solvent counterion. Rate constants for electron transfer between the molecule ion and a neutral molecule, which have been obtained for many pairs,[6–8] provide some test for theoretical models of electron transfer kinetics. Specific rates of proton transfer reactions of aromatic radical anions in polar protic liquids[4] have provided some examples of profound effects of the solvent[8] upon kinetics in solution.

For the radiation chemist, information has been obtained about the persistence, well into the chemical stage of events, of charge separation in irradiated polar liquids. In biological radiation reactions the role of molecular anions in electron-transfer processes has been demonstrated.[9] Evidence for the initial existence of heterogeneous ion pairs in the earlier physical stage of events, at times of less than 10^{-7} sec, has come from the observation[10,11] of ultrafast anion decay rates.

This Account deals with the homogeneous kinetics of aromatic molecule ions, with special emphasis on electron-transfer and proton-transfer reactions.

Mechanism of Formation

Irradiation, with high-energy electrons, of a solution of an aromatic compound in various organic liquids will generate the aromatic molecule ions. Depending upon the properties of the solvent and its purity, the aromatic molecule ion may have a sufficiently long lifetime to be observed by fast detection methods. In polar protic liquids, such as the aliphatic alcohols, the aromatic radical anion is formed[4] without any formation of the aromatic cation. In certain chlorinated hydrocarbons,[5,12] on the other hand, the aromatic cation is formed without any formation of the radical anion. In nonpolar aprotic liquids, such as cyclohexane,[10,13] both the radical anion and the cation of the aromatic molecule are formed.

In the aliphatic alcohols, irradiation with electrons of, *e.g.*, 1–10-MeV energy results initially in ionization

$$e^- + \mathrm{ROH} \longrightarrow \mathrm{ROH}^+ + 2e^- \qquad (1)$$

(eq 1). The secondary electrons produced in this step, in degrading to thermal energy, become solvated in polar liquids. The phenomenon of electron solvation was first recognized in the study of ammonia solutions[14] of alkali metals and since has been demonstrated for water[15] and for polar organic liquids[16] such as the alcohols.[17] The solvated electron will then attach to aromatic solute molecules such as naphthalene, anthra-

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cene, biphenyl, terphenyl, pyrene, etc. (if present at sufficiently high concentration) to form the radical anion (eq 2).

$$e_{sol}^- + \text{arene} \longrightarrow \text{arene}^- \qquad (2)$$

The solvent counterion, ROH^+, rapidly forms the alkyloxonium ion (eq 3). In these systems, the aromatic radical anion does not form an ion pair with the counterion. Indeed, the reaction with the counterion, which annihilates the anion (eq 4), has, as will be shown, a very high rate constant. This represents an important distinction in the form and behavior of the radical anion in these systems as compared with sodium solutions in tetrahydrofuran, in which the anion properties have been so extensively studied. In the sodium solutions (in which the counterion is Na^+) there is abundant evidence[18] that ion pairing of the aromatic radical anion with the sodium cation commonly occurs except at very low concentrations. No such ion-pair complex exists in the alcohol solutions, and the aromatic radical anion may therefore be regarded as a free anion—not, of course, free of solvation, but free of any cation complexing.

$$ROH^+ + ROH \rightleftharpoons ROH_2^+ + RO\cdot \qquad (3)$$

$$\text{arene}^- + ROH_2^+ \longrightarrow \text{areneH}\cdot + ROH \qquad (4)$$

In certain chlorinated hydrocarbon solvents such as 1,2-dichloroethane, aromatic radical cations are formed. Electron irradiation again causes ejection of an electron (eq 5). However, in these solvents, as the secondary electrons degrade to thermal energy, they become localized on chlorine atoms which have higher electron affinity than the aromatic molecules. This is probably a dissociative attachment process, for which there is evidence in other systems (eq 6). The aromatic solute molecule then transfers an electron to the positive charge center in the solvent to form the aromatic cation[5,12] (eq 7) provided the ionization potential of the aromatic molecule is lower than that of the dichloroethane. The counterion in this system is Cl^-, or possibly RCl^-.

$$e^- + RCl \longrightarrow RCl^+ + 2e^- \qquad (5)$$

$$e^- + RCl \longrightarrow R\cdot + Cl^- \qquad (6)$$

$$RCl^+ + \text{arene} \longrightarrow RCl + \text{arene}^+ \qquad (7)$$

Observation and Identification

By means of the pulse radiolysis technique, the aromatic anion or cation is formed, by reaction 2 or 7, respectively, in a time of 1 μsec or less, and may be observed during its lifetime. This fast reaction method, as described in review articles[2,19] and in a recent book,[3] uses an electron pulse of microsecond duration or shorter as the energy perturbation to initiate reaction, and, generally, fast optical absorption spectrophotometry to detect the reactive transients. At the time of the initial development of the technique, the electron pulse width commonly used was on the order of 1 μsec, with time resolution slightly better than 1 μsec. The technique has since been refined to the point where subnanosecond times have been resolved.[20]

The pulse current generally used is rather less than 1 A with a 1-μsec pulse, but may be somewhat higher with very much shorter pulses. This total pulse power is sufficient to produce initial concentrations of a particular reactive transient in the range of 10^{-5} to 10^{-4} *M*. A pulse current of 0.35 A with a 1.5-μsec pulse of 4-MeV electrons from an electron linear accelerator, as used in our laboratory,[21] produces an "initial" concentration of aromatic radical anions of about 2×10^{-5} *M* in an ethanol solution 0.1 m*M* in aromatic solute. Since much of the work described here involved electron pulses of 100- to 500-nsec duration, the concentration of aromatic radical anion produced was on the order of 1 μ*M* or somewhat higher.

Observation of the aromatic molecule ion by fast optical absorption spectroscopy and its identification from the observed absorption spectrum are then a relatively simple matter. Most of the aromatic molecule ions studied, in the particular solvents, exhibit a lifetime on the order of 1 μsec, or in some cases longer—a readily observable time range. The aromatic molecule ions have optical absorption spectra in the near-ultraviolet and in the visible region. Many of these spectra are well known from earlier studies[22,23] of sodium solutions in tetrahydrofuran containing aromatic molecules. In these solutions the aromatic radical anions are relatively stable so that the absorption spectra may then be determined by conventional methods.

Fast spectrophotometric detection of the absorption by the molecule ion at a convenient band presents the entire history of the ion, from the time of its formation during the electron pulse to its eventual disappearance by whatever reactions may occur. A typical example of such a rate curve showing the fast formation and subsequent decay of the diphenyl radical anion in an ethanol solution of diphenyl may be seen in Figure 1. From such rate curves, the absolute rate constants for a great many reactions have been determined. The decay curve in Figure 1, as will be described later, represents a proton transfer from the alcohol to the anion.

The absorption spectrum of the reactive transient may be determined by point mapping of the optical density at some fixed time, *e.g.*, zero time after the pulse, as a function of wavelength. Spectrophotographic recording has also been used. Figure 2 shows the optical absorption spectra of the molecule ions of biphenyl in various solvents. The spectrum of the anion obtained in a pulse-radiolyzed 2-propanol solution of

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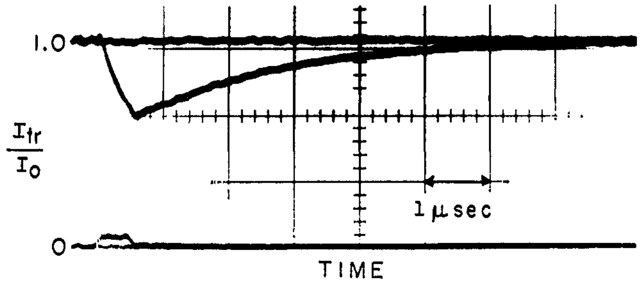

Figure 1. Rate curve for the decay of the biphenylide ion in pure ethanol containing biphenyl, observed at 620 nm. The pulse width is 500 nsec and the sweep time 1 μsec/div.

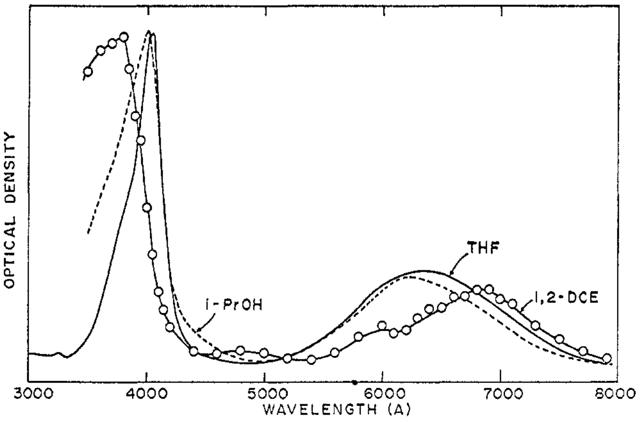

Figure 2. Optical absorption spectra of biphenyl molecule ions in various solvents. The spectra in 2-propanol and in tetrahydrofuran are that of the biphenyl radical anion; the spectrum in 1,2-dichloroethane is that of the biphenyl cation.

biphenyl is almost identical with that obtained from a sodium solution in tetrahydrofuran.

The spectrum of the aromatic molecule ion is sufficiently distinctive to distinguish the ion from electronically excited states or neutral free radicals. The spectrum alone does not permit one to discriminate between the anion and the cation since the electronic spectra of both anions and cations of alternant hydrocarbons, as expected on theoretical grounds, are nearly identical.[24] This discrimination may, however, be made with the use of various scavengers. Oxygen, for example, reacts very rapidly with the radical anion but is unreactive toward the cation. Aniline or ethanol at relatively low concentration removes the cation, but does not react with the anion. By combining the spectral information with data on scavenger effects, a reliable identification may be made.

Formation Rates

The formation of the aromatic radical anion, and of the cation, is very rapid at even moderate concentrations of the aromatic molecule in the types of system which have been described. With regard to the subsequent kinetics, the formation may be regarded as "instantaneous," that is to say it is complete at the end of the pulse, which may be as short as 100 nsec in some of this work.

Absolute rate constants for the formation of the radical anion in ethanol by the attachment reaction 2 have been determined[4] by observing the decay of the solvated electron. At 298°K, values for k_2 in ethanol range from $4.3 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ to $10.2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ for the aromatic compounds biphenyl, naphthalene, *p*-terphenyl, and naphthacene in increasing order. Thus, with a concentration of aromatic molecule of 0.5 m*M*, the half-time for the formation reaction is only 0.3 μsec or shorter depending on the compound.

Rate constants for the formation of the aromatic cation in 1,2-dichloroethane by reaction 7 are even higher.[5] Indeed, rate curves for reaction 7 could not be observed and values for k_7 were determined, from relative yields of the cation, to be $k_7 \geq 3 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$ for biphenyl at 298°K and $k_7 \geq 1 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$ for *p*-terphenyl at 244°K. These lower limiting values are fully threefold greater than the values of diffusion-controlled rate constants which have been determined experimentally. This comparison has led to the suggestion that the rate of reaction 7 cannot depend upon molecular transport of the positive charge center, and that transport of the hole (eq 8) may be a

$$\text{RCl}^+ + \text{RCl} \longrightarrow \text{RCl} + \text{RCl}^+ \qquad (8)$$

resonance charge-transfer process. This conclusion had been reached for the analogous reaction in low-temperature glasses.[25]

Decay of the Radical Anion by Proton Transfer

The aromatic radical anion in the aliphatic alcohols decays, apart from any reaction with possible impurities in solution, by two different types of proton-transfer reaction to form a hydrogen adduct free radical. The first is the reaction of the radical anion with the solvent counterion, reaction 4. This reaction has a very high rate constant[4] with values for k_4 in ethanol of 3.3×10^{10}, 3.7×10^{10}, and $1.9 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$ at 298°K for the biphenylide, anthracenide, and *p*-terphenylide ions, respectively. Although this reaction of the anion with hydrogen ion has such a high rate constant, it can, in most cases, be eliminated from competition with other elementary reactions by working at low concentration. Thus, at an anion concentration of 1 μ*M* and presumably the same concentration of counterion, the half-time for reaction 4 is longer than 30 μsec.

The other proton-transfer reaction in the aliphatic alcohols is transfer of a proton from the hydroxyl group of the alcohol itself (eq 9). The natural lifetime of the

$$\text{arene}^- + \text{ROH} \longrightarrow \text{areneH}\cdot + \text{RO}^- \qquad (9)$$

radical anion in the alcohol, that is, the lifetime at infinite dilution of anion and counterion in infinitely pure solvent, is determined by this reaction. Rate constants for reaction 9 have a relatively low value, but the reaction is nevertheless fairly rapid because of the high concentration of the alcohol. This is not a reaction of the anion with hydrogen ion from the autoionization of

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the alcohol; the equilibrium concentration of hydrogen ion is far too low. It is a reaction with the alcohol molecule itself in the hydrogen-bonded solvent structure.

The rate constants for reaction 9 depend upon the properties of the alcohol[4] (specifically the lability of the hydroxyl proton) and the nature of the aromatic radical anion.[26] The values of k_9 range over about three orders of magnitude for the systems studied, as may be seen from the following data.[4] Table I shows the first-order rate constants for reaction 9 for four different alcohols and three aromatic radical anions. The uncertainty in these values ranges from ±10 to ±25%. These rate constants may, of course, also be expressed in bimolecular units if one assumes the nominal monomer concentration to be valid. Thus, for reaction 9a

$$C_{12}H_{10}^- + CH_3OH \longrightarrow C_{12}H_{11}\cdot + CH_3O^- \qquad (9a)$$

the value $k_{9a} = 17 \times 10^5$ sec^{-1} converts to $k_{9a} = 6.9 \times 10^4\ M^{-1}$ sec^{-1}. The values for k_9 show a fairly close correlation with the acidity of the alcohol which varies over more than two orders of magnitude for the four alcohols in the table, as do the rate constants. This correlation supports the conclusion that the proton involved is that of the hydroxyl, not that of the alkyl group. The reaction of *p*-terphenylide ion with propanol is too slow to be measured (by this method) in competition with impurity reactions.

Table I

Values of k_9 (sec^{-1}) at 298°K

	Diphenylide	Anthracenide	*p*-Terphenylide
Methanol	17×10^5	20×10^5	0.09×10^5
Ethanol	4.4×10^5	4.0×10^5	0.04×10^4
1-Propanol	4.3×10^5	3.2×10^5	
2-Propanol	0.72×10^5	0.47×10^5	

Determination[26] of the temperature coefficient for reaction 9 indicates that the low values found for k_9 are not to be attributed to a high activation energy but rather to a low preexponential factor. The activation energy for the proton transfer from methanol and ethanol to anthracenide and diphenylide ion ranges from 2 to 3 kcal/mol, whereas the preexponential factor for these four cases ranges from 1×10^6 to $6 \times 10^6\ M^{-1}$ sec^{-1}. The proton-transfer reaction in 2-propanol has only a slightly higher activation energy, amounting to 6 kcal/mol with a preexponential factor of 3.2×10^8 and 1.5×10^8 for the two anions, respectively. Two physical phenomena involving solvent structure contribute to the low value for the rate constant. These are solvation of the anion, with the associated necessity for reorientation of the liquid structure when reaction occurs, and hydrogen bonding of the reactive proton. Some striking kinetic effects in two-component solvent systems, to be discussed later, provide interesting evidence of the importance of solvent structure.

Values for k_9 vary greatly with the particular aromatic radical anion.[26] Table II shows the proton-transfer constants in 2-propanol for a number of different radical anions. Even in this small sampling of aromatic compounds, values of k_9 range over more than two orders of magnitude. Particularly interesting is the large difference between *o*- and *m*-terphenyl on the one hand and *p*-terphenyl on the other. The much lower proton-transfer constant for *p*-terphenyl may reflect a greater degree of electron delocalization in this anion, but it is difficult to understand, on this basis, why the rate constant for biphenyl is not at least as large as for *o*- and *m*-terphenyl.

Table II

Values of k_9 in 2-Propanol at 298°K

Radical anion	k_9, sec^{-1}
Naphthalene	5.7×10^5
Phenanthrene	3.4×10^5
Biphenyl	0.72×10^5
Anthracene	0.47×10^5
o-Terphenyl	1.8×10^5
m-Terphenyl	1.4×10^5
p-Terphenyl	$<0.013 \times 10^5$

Electron-Transfer Rates

In solutions containing a single aromatic solute, the decay of the anion, as has been described, occurs through reactions 4 and 9. The rate of reaction 4 may be rendered negligible by working at very low concentration of the anion and the counterion. In certain of the alcohols, notably 2-propanol, the values for k_9 are so low that most of the aromatic radical anions have a lifetime ranging from several microseconds to several hundred microseconds. Similarly long anion lifetimes are also found in certain amines, if properly purified.

In such systems it has been possible, using the foregoing techniques, to determine accurately the absolute rate constants for the transfer of an electron from an aromatic radical anion to the neutral molecule of a different aromatic compound in solution (eq 10).

$$\text{arene}_1^- + \text{arene}_2 \underset{k_{10r}}{\overset{k_{10f}}{\rightleftharpoons}} \text{arene}_1 + \text{arene}_2^- \qquad (10)$$

Values for k_{10} have been determined for 13 donor–acceptor pairs in 2-propanol and for several pairs in other solvents. The electron-transfer rate constants may be evaluated in the following way.

If the concentrations of aromatic compounds in a two-component solute system are arranged with $[\text{arene}_1] \gg [\text{arene}_2]$ so that $k_2[\text{arene}_1] \gg k_2[\text{arene}_2]$, the anion of arene$_1$ will be formed preferentially over that of arene$_2$. If, additionally, the condition is imposed that [arene$_2$] is sufficiently high so that reaction 10 will be the rate-determining process in the disappearance of arene$_1$, the rate curve for this disappearance will be found to fit a first-order rate law, since $[A_2] \gg [A_1^-]$. There will be an additional upper limiting condition for [arene$_2$] since reaction 10 must not be too fast to be observable, nor indeed so fast that it overlaps with the ultrafast anion decay[10] which is thought to result from reaction of initial ion pairs in close proximity.

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A half-time of about 100 nsec or longer for reaction 10 meets this condition adequately. The differential rate expression for the disappearance of arene$_1$, under the most general of conditions, is

$$-\frac{d[A_1]}{dt} = -k_2[e_{sol}^-][A_1] + k_4[A_1^-][ROH_2^+] + k_9[A_1^-][ROH] + k_{10f}[A_1^-][A_2] - k_{10r}[A_2^-][A_1] \quad (11)$$

where k_{10f} is the rate constant for the forward and k_{10r} the rate constant for the reverse electron-transfer reaction. The first term in k_2 and the second term in k_4 are readily eliminated by appropriate selection of $[A_1]$ and $[A_1^-]$. The third term in k_9 may or may not be negligible, depending upon $[A_2]$ and the value of k_9, which, in turn, depends on the choice of solvent. If the difference in reduction potentials of the pair in reaction 10 is large, the rate of the reverse reaction will be negligible. k_{10f} may then be readily determined from the linear first-order plots of the decay curves. The more interesting cases are those for which the reverse reaction rate is not negligible. In that case, with the third term in eq 11 negligible, the integrated form of this equation is

$$[A_1^-]_t - [A_1^-]_e = ce^{-(k_{10f}[A_2] + k_{10r}[A_1])t} \quad (12)$$

where $[A_1^-]_t$ and $[A_1^-]_e$ are the concentrations of the donor anion at time t and at equilibrium, respectively. The function $(k_{10f}[A_2] + k_{10r}[A_1])$ may be obtained from linear plots of eq 12, and subsequent plots of this function against $[A_2]$ give k_{10f} from the slope and k_{10r} from the intercept. Such a plot is shown in Figure 3 for the electron transfer from pyrenide ion to anthracene in 2-propanol. The uncertainty in the value of k_{10f} is generally somewhat less than ±20%, that of k_{10r} about ±40%.

By similar methods, electron-transfer rate constants involving aromatic cations (eq 13) have been obtained

$$\text{arene}_1^+ + \text{arene}_2 \rightleftharpoons \text{arene}_1 + \text{arene}_2^+ \quad (13)$$

in 1,2-dichloroethane solution.[5] The electron donor in reaction 13 is, of course, the neutral molecule with the cation as acceptor, in contrast with reaction 10 in which the neutral molecule is the acceptor.

Values for k_{10}, some of which are listed in Table III, were obtained for 13 pairs in 2-propanol. Seven of these pairs: biphenyl$^-$ to anthracene, to pyrene, and to *p*-terphenyl, *p*-terphenyl$^-$ to anthracene and to pyrene, *o*-terphenyl$^-$ to pyrene, and *m*-terphenyl$^-$ to pyrene, have values in the range of 3×10^9 to 6×10^9 M^{-1} sec^{-1} at 298°K, at or very near the diffusion-controlled limit. The remainder fall below the diffusion-controlled limit, with the two lowest being two orders of magnitude lower. The rate constants for these two pairs, anthracene$^-$ to pyrene and 9,10-dimethylanthracene$^-$ to pyrene (for which the difference in the reduction potentials is positive), were determined as k_{10r}, the constant for the reverse reaction, as described.

In the case of transfer pairs for which both k_{10f} and k_{10r} have been determined, we may estimate the value of the equilibrium constant, K_e $(= k_{10f}/k_{10r})$, from these rate constants. For the pairs pyrene–anthracene and pyrene–9,10-dimethylanthracene the equilibrium constant values, at 298°K, are 86 and 35, respectively. These values may be compared with those obtained in tetrahydrofuran from potentiometric measurements,[27-30] which give values of 81 and 30 for the respective pairs. The agreement is quite good.

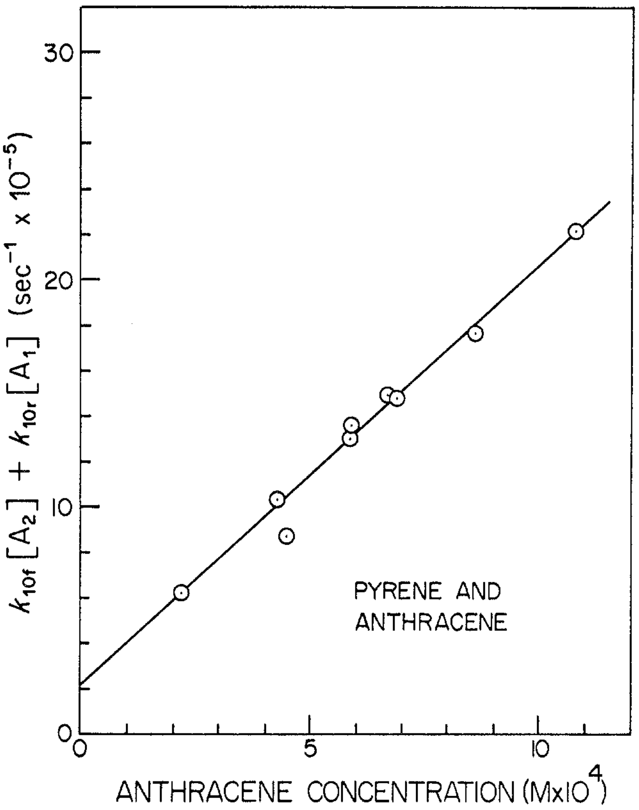

Figure 3. Plot of the function $(k_{10f}[A_2] + k_{10r}[A_1])$ against concentration of 9,10-dimethylanthracene for the transfer pair pyrene–dimethylanthracene. The concentration of pyrene is constant and equal to 1.1×10^{-2} M. The value of k_{10f} is obtained from the slope, the value of k_{10r} from the intercept.

These data for 2-propanol[7] as solvent, and other data for other solvents,[8] have been used to test the validity, at least semiquantitatively, of the theory of Marcus[31-38] for electron-transfer rates. In this model, the free energy of activation, ΔF^*, which determines the rate constant for an activation-controlled electron-transfer reaction (eq 14) is given by eq 15. $\Delta F°$ is the standard

$$k_{act} = Ze^{-\Delta F^*/RT} \quad (14)$$

$$\Delta F^* = w + \frac{\lambda}{4} + \frac{\Delta F°}{2} + \frac{(\Delta F°)^2}{4\lambda} \quad (15)$$

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Table III

Values for k_{10} (M^{-1} sec^{-1}) in 2-Propanol at 298°K

Donor–acceptor pair	k_{10}	$\Delta F°$, kcal/mol	k_{act}	$(k_{act})_n/(k_{act})_1$	$(k_{act}^{calcd})_n/(k_{act}^{calcd})_1$
Anthracene$^-$–pyrene	2.1×10^7	+2.61	2.1×10^7	0.081	0.041
9,10-Dimethylanthracene$^-$–pyrene	3.7×10^7	+2.01	3.7×10^7	0.14	0.074
Diphenyl$^-$–naphthalene	2.6×10^8	−0.99	2.7×10^8	1.0	1.0
Diphenyl$^-$–phenanthrene	6×10^8	−3.28	6.7×10^8	2.6	5.3
Pyrene$^-$–9,10-dimethylanthracene	1.3×10^9	−2.01	1.7×10^9	6.5	2.2
Pyrene$^-$–anthracene	1.8×10^9	−2.61	2.6×10^9	10.1	3.4
Diphenyl$^-$–pyrene	5.0×10^9	−12.2			
Diphenyl$^-$–anthracene	6.4×10^9	−14.8			

free energy of the reaction, which is taken as the difference in reduction potentials of the donor–acceptor pair. The solvent reorganization parameter, λ, is a function of the dielectric properties of the solvent (eq 16), where

$$\lambda = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{D_{op}} - \frac{V}{D_s}\right)(\Delta e)^2 \qquad (16)$$

D_{op} is the optical dielectric constant and D_s is the static dielectric constant. The effective radii for the encounter, a_1 and a_2, include a monolayer of solvent around the anion in addition to the molecular radii; r is taken as $a_1 + a_2$. Δe, the change in charge of the donor, is +1 for these systems. w, the difference in work of bringing together reactants and separating products, is small in these systems, since one reactant is uncharged, and w is therefore neglected. It is assumed that the contribution to λ from inner reorganization (reorganization of bonds in the reactants) is small for aromatic compounds.

Table III contains, in addition to the absolute value for k_{10} found experimentally, the value for k_{act} from eq 17, taking k_{diff}, the limiting value for diffusion-con-

$$\frac{1}{k_{10}} = \frac{1}{k_{diff}} + \frac{1}{k_{act}} \qquad (17)$$

trolled reactions, as 5.7×10^9 M^{-1} sec^{-1} from experimental values. A test of the validity of the Marcus theory is made by comparing $(k_{act})_n/(k_{act})_1$, the experimental value of k_{act} obtained from (17) and normalized relative to the pair diphenyl$^-$–naphthalene, with $(k_{act}^{calcd})_n/(k_{act}^{calcd})_1$, the value calculated from eq 14–16, normalized in the same way. The calculated value for k_{act} is for λ = 16 kcal/mol, obtained from (16) taking $a_1 = a_2 = 5$ Å. The normalization simply removes the value of Z from consideration in this comparison by assuming that the collision number is approximately the same for all the pairs and cancels out. Examination of the last two columns of Table III, which includes electron-transfer constants ranging over two orders of magnitude, shows a fairly good semiquantitative correlation between theory and experiment on this relative basis. To be sure, the test of the dependence upon solvent properties in this series is limited to a single solvent, 2-propanol, and appears as a constant, λ = 16 kcal/mol, rather than as a variable.

An attempt to test the dependence upon solvent properties separately has recently been made[8] from data in ethanol, ethylenediamine, and diethylamine in addition to 2-propanol. The rate constant for the pair pyrene$^-$ to 9,10-dimethylanthracene has been determined in all four solvents. The data are shown in Figure 4 which presents a plot of log k_{act} as a function of λ. The straight line is drawn from the Marcus theory for the same value of a_1 and a_2 used in Table III. There is no doubt that k_{act} increases in the direction predicted by the model, and perhaps it is justifiable to conclude that the data, for this limited series, again support the theoretical model on a semiquantitative basis.

Electron-transfer constants have also been obtained for three aromatic cation–molecule pairs in 1,2-dichloroethane. Values of k_{13} are given in Table IV. No adequate test of the theory may be drawn from such limited data, but it is of interest to point out that the Marcus theory predicts, for this solvent, that $k_{13} = k_{diff}$ if $\Delta F°$ is more negative than about −0.4 eV. A conjectural theory exists for proton transfer,[39–41] but the data from the present work are not yet extensive enough to serve as an adequate test of the model.

Table IV

Values for k_{13} (M^{-1} sec^{-1}) in 1,2-Dichloroethane at 298°K

Acceptor cation	Donor molecule	k_{13}	Ionization potential difference, eV
Biphenyl$^+$	Pyrene	9.9×10^9	−1.4
p-Terphenyl$^+$	Anthracene	8.1×10^9	−1.2
Diphenyl$^+$	*p*-Terphenyl	5.1×10^9	−0.17

Solvent Effects on Proton-Transfer Rates

The values for k_9, the proton-transfer constant of the aromatic radical anions, discussed in an earlier section, had all been obtained for one-component solvent systems. The solvent was, in all cases, an aliphatic alcohol. Recent results[8] from studies in two-component solvent systems have demonstrated very large effects of the solvent upon k_9, effects which are related to the solvent structure-making and solvent structure-breaking properties of the added component. All of these recent investigations of solvent effects have been based on the reaction of the diphenylide ion with ethanol (eq 9b).

$$C_{12}H_{10}^- + C_2H_5OH \longrightarrow C_{12}H_{11}\cdot + C_2H_5O^- \qquad (9b)$$

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(39) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).

(40) A. O. Cohen and R. A. Marcus, *ibid.*, **72**, 4249 (1968).

(41) R. A. Marcus, *J. Amer. Chem. Soc.*, **91**, 7224 (1969).

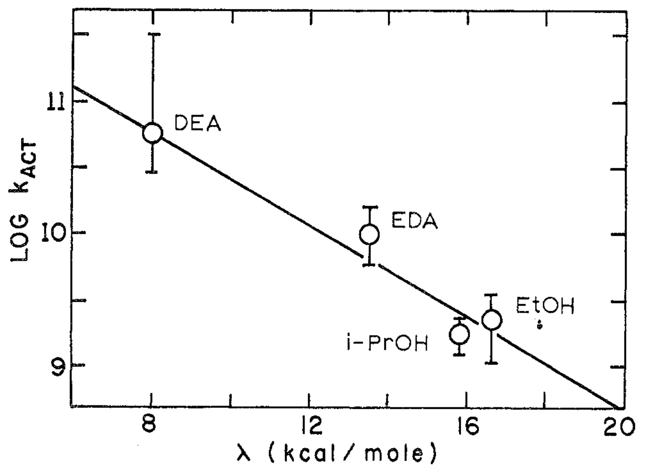


Figure 4. Plot of log k_{act} against λ for the electron transfer from pyrene⁻ to 9,10-dimethylanthracene. The straight line is calculated from the Marcus theory with the same values for the parameters used in the calculation of Table III and with an arbitrary reference point on the ordinate scale. The solvents are diethylamine (DEA), ethylenediamine (EDA), 2-propanol (*i*-PrOH), and ethanol (EtOH).

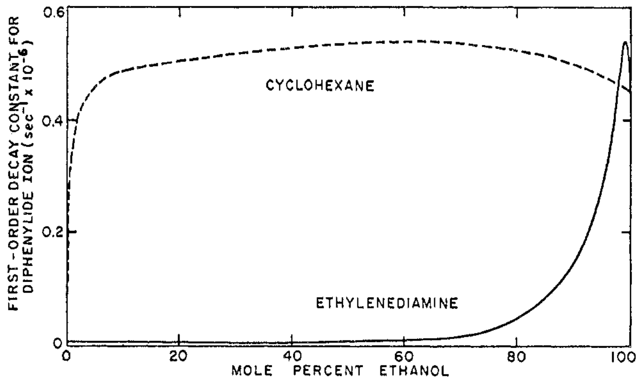
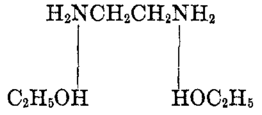


Figure 5. First-order constant for the decay of the biphenylide ion in two-component solvent systems, with ethanol as one of the solvents, as a function of mole per cent ethanol. The data shown are for ethylenediamine (—) and cyclohexane (- - -) as the second solvent.

The rate constant for this reaction in ethanol as solvent is $k_{9b} = 4.4 \times 10^5\ \text{sec}^{-1}$ at 298°K. Irradiation of biphenyl solutions in many other polar solvents such as ethylenediamine and triethylamine will also form the biphenylide ion. The lifetime of $C_{12}H_{10}^-$ in ethylenediamine, however, is fully 100 times greater than in ethanol, provided the solvent has been properly purified. This very slow decay of the biphenylide ion in ethylenediamine probably occurs partly through reaction with the counterion and partly by reaction with impurity. It is not known whether there is any proton transfer from the ethylenediamine. The proton-transfer reaction with ethanol, reaction 9b, when carried out in ethylenediamine as solvent with ethanol added, shows a profoundly lower specific rate[8] compared with the reactivity in ethanol alone. This may be seen in Figure 5, in which the first-order constant for the decay of the biphenylide ion is plotted as a function of composition in the two-component system ethylenediamine–ethanol. As the concentration of ethanol in ethylenediamine is increased, the lifetime of the biphenylide ion remains virtually unchanged until a concentration of some 65 mol % ethanol is exceeded. Reaction 9b thus appears to be essentially completely inhibited in ethylenediamine solution, *i.e.*, k_{9b}, which has the value $4.4 \times 10^5\ \text{sec}^{-1}$ in pure ethanol, becomes vanishingly small in ethylenediamine solvent. Two separate phenomena may contribute to this large effect of the solvent upon the specific rate of the proton transfer reaction: differences in solvation of the radical anion and extensive hydrogen bonding of the reactive alcohol proton to the amine—hydrogen bonding which is stronger than in the pure alcohol. The existence in solution of a hydrogen-bonded complex appears to have diverse effects which cannot be discussed here because of space limitation, but it is of interest to point out that the protonation reaction with ethylene glycol,[8] which shows a similar effect, exhibits a break in the horizontal portion of the curve much closer to 50 mol % for the dihydric alcohol, compared with 65 mol % for ethanol.



$$\begin{array}{ccc} & H_2NCH_2CH_2NH_2 & \\ & | \qquad\qquad | & \\ C_2H_5OH & & HOC_2H_5 \end{array}$$

Compounds which affect the solvent structure may, of course, accelerate the proton transfer[8] as well as inhibit the reaction. Thus, if cyclohexane is the second component which serves as diluent, the value of k_{9b} may be seen (Figure 5) to increase as the mole per cent of cyclohexane increases. In the region of 30 mol % ethanol, this represents an increase in the value of k_{9b} of about an order of magnitude. Comparing the overall effect of these two solvents, combined separately with ethanol, it may be seen that k_{9b} is changed over a range of three orders of magnitude. The proton-transfer reaction thus serves as a useful probe for the study of solvent effect in chemical kinetics, many complexities of which are not yet fully understood.

The fast reaction method which has been used in these studies is an extremely effective technique for the investigation of the chemistry of organic molecule ions involved in their decay kinetics as free ions in highly reactive solvents.

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