SOLVENT EFFECTS ON THE KINETICS OF ELECTRON AND PROTON TRANSFER REACTIONS OF AROMATIC RADICAL ANIONS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By
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* * * * *

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INTRODUCTION

Electron and proton transfer reactions are among the most fundamental solution reactions. The space devoted to these reactions in a number of recent reviews on fast reactions in solution (1, 2) is an indication of their importance in redox chemistry, in acid-base catalysis (3), and in the elucidation of complex reaction mechanisms in general. Of particular importance are their roles in enzyme processes in biological systems (4).

Aromatic radical anions, aside from their intrinsic interest, are useful as model systems in studies of electron and proton transfer reactions. This is due in part to the ease with which they can be identified by their optical absorption spectra in the near-infrared to near-ultraviolet region of the spectrum (5, 6, 7). It is also due in part to the ease with which their kinetic behavior can be monitored by optical absorption spectrophotometry.

The techniques of pulse radiolysis are especially useful to the study of the kinetics of the reactions of the aromatic radical anions, since in irradiated polar liquids the behavior of the radical anions does not depend on their existence as ion-pairs, but only on their properties as solvated anions. By contrast, in sodium solutions in tetrahydrofuran containing aromatic compounds, the anions, depending on their concentrations, may be associated with the alkali metal cations (8).
If a $10^{-2}$M solution of an appropriate aromatic compound in a simple aliphatic alcohol is irradiated, the ratio of the electron density of the solvent to that of the solute is such that essentially all ionization processes involve the solvent:

$$e^- + \text{ROH} \rightarrow \text{ROH}^+ + 2e^- \quad (1)$$

The positive ion in solution presumably exists in the form of the alkyloxonium ion, $\text{ROH}_2^+$ (5), and the electrons, as they become collisionally degraded to thermal energies, are solvated. Solvation of electrons by polar liquids such as the alcohols (9) and the amines (10) is a well-known phenomenon in pulse radiolysis studies. An important part of the identification of the aromatic radical anions is the observation that their precursor is the solvated electron (5):

$$e_{\text{sol}}^- + \text{A} \rightarrow \text{A}^- \quad (2)$$

Specific rate constants for the formation of the radical anion by reaction 2 and for the decay by recombination with the alkyloxonium ion,

$$\text{A}^- + \text{ROH}_2^+ \rightarrow \text{AH}^- + \text{ROH} \quad (3)$$

were determined (5) for a number of radical anions in ethanol.

Specific rate constants were determined for the protonation of the radical anions by the alcohol,

$$\text{A}^- + \text{ROH} \rightarrow \text{AH}^- + \text{RO}^- \quad (4)$$

for a number of anions in the simple aliphatic alcohols (5), and the temperature dependence of these rate constants was determined in some cases (11).

In isopropanol, specific rate constants for the transfer of an electron from the aromatic radical anion to a neutral (different)
aromatic molecule,

\[ A_1^- + A_2 \xrightarrow{k_p} \frac{k_p}{k_r} A_1 + A_2^- \quad (5) \]

were determined for a number of pairs (12, 13). A correlation was shown (13) on a relative basis with a theory (14-21) which predicts an exponential dependence of the rate constant on the difference in reduction potential between the neutral aromatic compounds in the donor-acceptor pair.

The portion of this study which is concerned with electron transfer reactions is directed toward the determination of the absolute kinetics of electron transfers from some aromatic radical anions to neutral, different aromatic molecules in various solvents. An aim of this study is the investigation of solvent effects on the specific rate constants for these transfers. Some test is provided by these data for a theoretical model (14-21) which takes solvation effects into account, and which predicts a dependence of the specific rate constant for an electron transfer reaction on the dielectric properties of the solvent used.

The portion of this study concerned with proton transfer reactions is directed toward the investigation of the effects of solvent-solvent interactions on the kinetics of protonations of the biphenylide radical anion by some alcohols in mixed-solvent systems.
EXPERIMENTAL

The general techniques of pulse radiolysis, described below and elsewhere (22) were employed for this study.

PULSE IRRADIATION

A Varian V7715A linear electron accelerator was used as a source of high-energy electrons. It is capable of producing electron pulses which can be continuously varied from about 50 nanoseconds to 1.4 microseconds, with currents of about 325 ma. In another operating mode 600 ma pulses from 20 to 140 nsec can be obtained, but this mode was not used in this study. The electron energies can be varied from 2 to 6 MeV, but only electrons in the 3 to 4 MeV range were used in this study. Pulse lengths used ranged from 100 to 500 nanoseconds.

Time profiles for two pulses are given in Figure 1. The rise and decay times of the pulse, independent of pulse width, are 6 nsec; thus, the end of energy deposition into the cell is clearly defined. A 200 nsec pulse at 325 ma delivers a dose in water of approximately $1.2 \times 10^{17}$ ev/g (23); a precise measure is not needed for this study.

The irradiation cell used is made of fused quartz, with optical windows of high purity silica to minimize coloration by irradiation. Internal dimensions of the cell are: 20 mm in the direction of the analyzing light beam (perpendicular to the electron beam), 12 mm vertically, and 8 mm deep, i.e., in the direction of the electron beam. The sides of the cell are approximately 1 mm thick.
Figure 1: Time profiles of two 325 ma electron pulses.
It was found (24) that the radiation received by the solution through the quartz wall is approximately uniform over its entire area in the plane perpendicular to the electron beam. Furthermore, the dose absorbed by ethanol is approximately uniform through the depth of the cell, the last 2 mm absorbing 90% of the amount of radiation absorbed by the first 2 mm (24).

The effects of a non-uniform distribution of reactants on the measurement of a rate constant by the methods of this study have been discussed (25, 26). For a first-order or pseudo-first-order constant, non-uniformity in dose absorbed across the light beam will cause an error in the rate constant of less than one percent. For a second-order rate constant, whose value also depends on the distribution along the light path, the error will be at most a few percent (26), which is small compared to other errors involved in the determination of the second-order rate constants in this study.

The cell is generally connected, through a tube (6 mm I.D.) with a graded seal, to a pyrex storage bulb, the volume of which is large (25 ml or greater) relative to the cell volume. Thorough mixing of the solution following each pulse minimized any interference with the decay kinetics of the radical anions by stable radiolysis products formed. Even when several pulses were used between mixing, little, if any, effect on the decay kinetics was noted.

The temperature of the cell was usually the ambient temperature of the radiation room, which was kept constant within ±1 degree centigrade. In some of the mixed-solvent experiments, the temperature regulation was no better than ±3 to 4 degrees centigrade, due to the
method used to add a second solvent, as will be described.

OPTICAL DETECTION

Fast spectrophotometric observation of the optical density of the solution was used to monitor the concentration of aromatic radical anions. A schematic of the optical detection system used is shown in Figure 2. The analyzing light source was an Osram 500-watt xenon lamp (Type XB0450W). Its output was constant to within ±1% during the time of any measurement and was usually stable for minutes. A remote-controlled shutter and appropriate Corning filters were used to minimize photodecomposition of the solution by the analyzing light, which struck the cell for only a few seconds at the time of the pulse. The analyzing light passed twice through the cell at the time of the pulse. After passing through an appropriate Corning filter it was focused into a Baush and Lomb grating monochromater. Grating types used were: Type 33-87-07, wavelength region 200-700 nm, 1200 grooves/nm, dispersion of 7.4 nm per mm of exit slit width; Type 33-86-02, 350-800 nm, 1350 grooves/nm, 6.4 nm/mm; and Type 33-86-03, 700-1600 nm, 675 grooves/nm, 12.8 nm/mm.

The light exiting the monochromator impinged upon the photo-cathode of a photomultiplier tube. RCA tubes numbered 7200, 1-P28 and 7102, with S-19, S-5 and S-1 responses, respectively, were used in this study. The output of the photomultiplier tube was coupled through a signal conditioning amplifier (Nexus Model FSL12) and a 93-ohm shielded transmission cable to a dual-trace oscilloscope. The total light intensity was adjusted by the widths of the entrance and exit slits of the monochromator.
Figure 2:— Schematic diagram of the optical arrangement.
in such a way that the amplifier output was generally less than 0.75 volts, well within the linear response region of the Nexus amplifier. The linearity of the amplifier was checked from time to time through the use of a low-intensity gallium arsenide lamp. The output pulse from this lamp was superimposed on the output from a continuous high-intensity source. The pulse height was seen to remain constant as the total output was increased to about 1.5 volts.

For point by point spectral mapping, the light beam was split with a partially reflecting chromium on quartz mirror and focused into two monochromators. One wave-length was then used as a reference standard, to normalize any variation in pulse intensity from pulse to pulse, while the other wavelength was varied. It was also possible to monitor the optical density changes of the solution at two wavelengths using the split light beam.

The signal from the amplifier was displayed on the screen of a dual-beam oscilloscope (Tektronix Type 555), which allowed the monitoring of the signal at two different sweeps, or at different wave-lengths, or both. The traces on the screen were photographed with an oscilloscope camera (Tektronix C-12 Polaroid) using Polaroid film (Type 107, 3000 speed).

The vertical scale of the oscilloscope was calibrated using an internal calibration voltage before each run, and this calibration was checked periodically during the run. Since optical density measurements depend only on light intensity ratios, absolute vertical calibration is unnecessary. If an expanded scale is used on one channel of the oscilloscope, however, the ratio of the vertical sensitivities had to be
known. The time base was calibrated frequently and found to be stable over a period of several months (26). The horizontal sweep was linear with time over the middle eight centimeters of the screen to within ±2.5%.

The response time of the entire system was short enough that a signal, changing exponentially with a half-life of 200 nsec. could be followed to within ±1% by the detection system. Experimental conditions could usually be adjusted to insure that the kinetics were at least this slow.

MATERIALS

The ethanol (U. S. Industrial Chemical Company) used in this study was purified occasionally as follows: 5 g of magnesium turnings and 0.5 g iodine were put into a 1 liter flask, followed by 50-75 ml ethanol. The mixture was warmed until magnesium ethoxide was formed (vigorous reaction). About 500 ml of ethanol were added, refluxed for an hour, and distilled.

The decay kinetics and initial yields of the aromatic radical anions were usually the same whether the alcohol was purified or not; therefore, in most cases, the ethanol was used without further purification.

The ethyleneglycol (Matheson, Coleman and Bell reagent grade) was used without further purification. The protonation reaction of biphenylide radical anion in ethyleneglycol exhibited essentially the same kinetic behavior with or without extensive purification (27).

The ethylenediamine (Baker Chemical Company reagent grade) was
purified as follows: about a 600 ml quantity was refluxed with 30-35 g of sodium (Allied Chemicals) or potassium (Baker) for an hour, or alternatively, with lithium aluminum hydride (Ventron) for about twenty minutes. The ethylenediamine was distilled and the middle 350 ml were collected in a 500-ml round bottom flask through a Fisher and Porter 4-mm quick-opening valve (no. 795-005) with a Teflon plug. In most instances, the reflux and distillation took place under a nitrogen atmosphere. The flask was then connected to the vacuum system by a Fisher and Porter 9-mm 0-ring joint (no. 571-190). These stopcocks and joints were used exclusively in all experiments. The flask was then cooled for approximately 1-2 minutes in liquid nitrogen. The stopcock was opened and the ethylenediamine was degassed by pumping with a vacuum and shaking the flask vigorously at the same time. After about 5 minutes, the ethylenediamine was vacuum distilled into a similar flask inside of which was a mirror of triply-distilled potassium. After a few hours or less, a blue color developed, indicating formation of solvated electrons from dissolved potassium metal.

Diethylamine (Baker Analyzed Reagent) and triethylamine (Matheson, Coleman and Bell) were purified in the same way as ethylenediamine, but no color developed.

Cyclohexane (Phillips Petroleum Company research grade), rated 99.98% pure by the manufacturer, was used without further purification.

Water was triply distilled in a quartz still. The first two distillations were from acid dichromate solution and basic permanganate solution, respectively.

Biphenyl, naphthalene, phenanthrene, and pyrene (James Hinton, New-
port News, Va.), had been zone refined and were rated as follows:
biphenyl and naphthalene, 99.99% pure; phenanthrene, 99.999% pure; and
pyrene, 99.8% pure. These aromatic compounds were used without purifi-
cation. The 9,10-dimethylanthracene, obtained from K and K Labs,
Incorporated, was recrystallized from isopropanol solution.

SOLUTION PREPARATION

For studies of electron transfer reactions from aromatic radical
anions to different, neutral aromatic molecules:

\[ A_1^- + A_2 \xrightarrow{k_r} A_1 + A_2^- \]  \hspace{1cm} (5)

where \( A_1 \) is one aromatic compound and \( A_2 \) another, the method of deter-
mining a specific rate constant \( k_r \), as will be described, requires that
the concentration of \( A_2 \) be varied during a "run" while that of \( A_1 \) be held
fixed. The two methods of solution preparation described below are used
for a number of reasons. Solvent purification methods involving the use
of potassium mirrors make it necessary that the solutions be prepared
under vacuum, and the concentrations of \( A_2 \), which determine the reaction
velocity, range from \( 10^{-5} \) to \( 10^{-3} \) M. The first criterion rules out the
usual pipet-dilution method of preparing solutions of low concentration.

Both methods described below have the advantage that there will be
no variation during the run due to solvent impurity reactions or to
variations in \( A_1 \) concentration, since only one cell is used throughout
the run, with the same solvent-\( A_1 \) solution. In contrast, normal prep-
paration procedures yield a number of cells for each run, each having
different \( A_2 \) concentrations and approximately the same \( A_1 \) concentrations.
(The term "cell" refers hereafter to the entire apparatus of irradiation
cell, connected bulbs, and sidearms.) Since the rate constants for the
electron transfer reactions are determined from differences in the
kinetics of the radical anions with changes in \( A_2 \) concentration, as will
be described, this advantage is important.

The "bulb technique," developed by Dye (28) was used for most of
the systems. The cell designed and used for this work is shown in
Figure 3. The acceptor aromatic compound, \( A_2 \), was introduced into small,
thin-walled pyrex bulbs (usually having radii of 5 to 6 mm), which had
been weighed. The bulbs were then degassed, sealed, and reweighed. Cor-
rection factors for the weight of air in the bulbs at the first weighing
were used to determine the weight of \( A_2 \). This factor in a few cases
amounted to as much as 50% of the total weight difference, and in these
cases, the actual uncertainty in solute weight reached as much as \( \pm 30\% \).
In general, however, the errors were much less than this. The bulbs were
then placed in the bulb storage sidearm in inverse order to that in
which they were to be broken. A one-inch magnetic stirring bar was fixed
into position at the mouth of the sidearm by a U-magnet taped onto the
outside of the cell. This stirring bar served not only to hold the bulbs
in position through the subsequent cleaning and solution preparation,
but it also was used during the run to break the bulbs one at a time.
The stirring bar could literally be "thrown" onto a bulb in the appro-
priate arm through the use of the U-magnet.

The cell was then washed with a solution of 25 ml hydrofluoric acid,
100 ml nitric acid, 10 g Alkonox detergent, and 300 ml water. After a
number of rinses, including one with a nitric acid-hydrogen peroxide
(approximate volume ratio 50:1) solution, the cell was closed at the
Figure 3:— Cell used for studies of electron transfer reactions by the "bulb" method.
0-ring joint, connected to the vacuum line, and flamed under vacuum.

The donor aromatic compound, $A_1$, was weighed and introduced through the stopcock into the storage bulb. The cell was then evacuated, weighed, and reconnected to the vacuum line. The solvent was then vacuum distilled from a reservoir of purified, degassed liquid into the storage bulb. The volume added was determined from the weight difference and the density.

This technique allows one to add various amounts of a solute, in this case, $A_2$, to a solution of known composition, in this work a solution of constant concentration in $A_1$, by simply breaking the bulbs individually.

The second method of solution preparation used for the electron transfer studies was a dilution technique. Although it was used only in the determination of one specific rate constant, its usefulness is general when smaller concentrations of a solute need to be added to a solution of constant composition in another solute. The cell used is shown in Figure 4.

After being thoroughly cleaned and dried as in the previous case, the cell was opened at the O-ring joint, through which a weighed amount of $A_2$ was introduced into storage chamber B, the volume of which was calibrated. The cell was then reconnected at the O-ring joint, D, evacuated, and the stopcock at E was closed. $A_1$ was weighed and introduced into the storage bulb A through the stopcock at F. The cell was then evacuated, weighed, and reconnected to the vacuum system. Solvent was then vacuum distilled from a reservoir into the storage chamber A, and its volume determined from the weight difference. Stopcock E was
Figure 4:-- Dilution cell designed for electron transfer studies.
opened and the solution was poured into the chamber containing $A_2$ to a known volume. Stopcock E was then closed. The total solution in the cell was fixed in $A_1$ concentration, and storage bulb B also contained a known concentration of $A_2$. Stopcock E was opened carefully, and a known volume of solution was poured from B into the graduated 1-ml side-arm, C. It was possible, in this way, to add $A_2$ to the solution in $A$ such that

$$[A_2]_A = \frac{V_C}{V_A^0 + V_C} [A_2]_B$$

where $[A_2]_A$ and $[A_2]_B$ are the concentrations of $A_2$ in storage arms $A$ and $B$, respectively, and $V_A^0$ is the volume of arm $A$ before the addition. Since the volume generally poured into arm C was 0.5-1 ml, and the volume of A was approximately 60 ml, the concentration of $A_2$ was reduced by a factor of about two orders of magnitude. By this technique, it was possible to add known (small) amounts of $A_2$ during a run to a solution of constant concentration in $A_1$.

Solutions for studies of proton transfer reactions were normally prepared in a simple cell assembly consisting of the irradiation cell and a 50 ml storage bulb, which could be connected to the vacuum system through a teflon stopcock and an O-ring joint. After the cell was cleaned and dried as previously described, the aromatic compound was weighed and introduced through the stopcock into the storage bulb. Biphenyl, $\phi_2$, was used exclusively in the proton transfer work. The cell was then evacuated, weighed, and reconnected to the vacuum system. The primary solvent was vacuum distilled from a reservoir into the storage bulb. The weight difference gave the amount of solvent present,
and hence the $\phi_2$ concentration, a precise knowledge of which was not important. During the run, the total solvent composition was varied by the addition of a second solvent, from a different reservoir, by vacuum distillation into the storage bulb, the contents of which were frozen with liquid nitrogen. The amount of second solvent added was determined from the difference in weight before and after each addition.

Ethylene glycol is viscous and not readily degassable by the usual technique of shaking vigorously while pumping with a vacuum. It is also not easily transferable by vacuum distillation. For these reasons, two other types of cell were used in experiments involving ethylene glycol. All three types are shown in Figure 5. Ethylene glycol solutions of biphenyl in storage arm A of Cell II, or arm B of Cell III, were deaerated by bubbling argon gas through the fritted glass discs for 15 to 20 minutes. The cells were then pumped by vacuum for about 5 minutes to remove most of the argon. This facilitated the subsequent additions to Cell II of a secondary solvent by vacuum distillation. The composition after each addition was again determined from the weight difference. In Cell III, the glycol was added in 0.5ml portions, as measured by the volume between the two stopcocks C and D, to a prepared solution of biphenyl in the primary solvent. The volume of ethylene glycol added and its density were used to determine the solvent composition after each addition.

**DATA ANALYSIS**

Rate curves were analyzed as twice enlarged photostatic prints of pictures taken of the oscilloscope screen. The quality of the enlarge-
Figure 5:-- Cells used for studies of proton transfer reactions.
ments was checked by looking for distortion in the grid lines from the oscilloscope screen. Vertical and horizontal measurements were made by placing a grid (0.05 inch) over the print on a glow-box.

A representative print is reproduced in Figure 6. The horizontal line labeled 0% was written by the oscilloscope when the lamp shutter was closed. That no long-lived emitting species were produced by the pulse can be seen from the 0% line, which shows that the emission produced during the pulse decays rapidly at the end of the pulse. Generally, the width and shape of the time profile of the emitted light signal was found to correspond closely with that of the electron pulse (Figure 1), as monitored before each day's run by a coaxial collector. The I₀ horizontal line is a measure of the light transmitted through the system before a pulse. Five milliseconds after the oscilloscope wrote the I₀ line the electron pulse was automatically triggered, and the transmitted light, Iₜₐᵣ, at the wavelength set by the monochromator was recorded as a function of time. The lower channel of the oscilloscope wrote a similar set of traces, but at a selected faster sweep speed.

The optical density at a given wavelength is defined as:

\[ D_t = \log \left( \frac{I_0}{I_{tr}} \right) \]  

If the Beer-lambert Law is obeyed for a single absorbing species, A, then

\[ D_t = e_A \cdot d \cdot [A] \]  

where [A] is the concentration of species A at time t, in molar units, d is the length of the light path in cm, and \( e_A \) is the decadic molar extinction coefficient, the value of which depends on the wavelength used and the species A.
Figure 6: Rate curves for the decay of the biphenylide ion in ethanol at 620 nanometers.
In the derivation of Equation II it is assumed that there are no interactions of absorbing species A with each other. Since the concentrations of absorbing species in this study are micromolar, and since these species have like charges, association is unlikely. The derivation also assumes that the light is strictly monochromatic. The bandwidths actually used were generally kept below 10 nm, as determined by the dispersion characteristics of the monochromator grating used and the width of the exit slit of the monochromator. The absorption bands of the radical anions of this study are generally broad (6, 7) so that the extinction coefficient can be assumed to be nearly constant over the narrow bandwidths used. Confidence in the use of Equation II comes from the fact that the kinetics of first-order reactions of the radical anions as measured by optical density changes are independent of wavelength used in the region of the absorption maxima of the species. Scattered light, which would give anomalously high values for \( I_0 \) and \( I_{itr} \), and hence low values for \( I_0/I_{itr} \), was found to be less than 2% of \( I_0 \).

The prints, then, give a value for the optical density, or the product \( \epsilon_A[A]d \) as a function of time. For most of this study, only the optical density (or this product) was needed. In the one instance where an absolute concentration was needed, the extinction coefficient was obtained from other work.

If the absorption of a species was small, the vertical scale of one of the channels of the oscilloscope was expanded electronically by a factor of 2, 5, or 10, and the other channel was used to determine \( I_0 \). The accuracy of \( I_0 \) determined in this manner was valid to within ±5%. 

RESULTS AND DISCUSSION

Specific rate constants for the electron transfer reaction from the radical anion of one aromatic compound to the neutral molecule of a different aromatic compound have been determined for the following pairs of aromatic compounds in the following solvents: biphenyl-naphthalene and pyrene-9,10-dimethylantracene in ethanol; biphenyl-naphthalene, pyrene-9,10-dimethylantracene, and biphenyl-phenanthrene in ethylenediamine; and pyrene-9,10-dimethylantracene in diethylamine. The selection of these pairs was based on the fact that there is no appreciable spectral overlap by at least one of the anions of the pair with the optical absorption spectrum of the other. Another consideration was that the electron transfer reactions are largely activation-controlled (as opposed to diffusion-controlled) as was reported (13) for these pairs in isopropanol. Solvent selection depended on the dielectric properties and purification requirements of the solvents considered.

A correlation of the results for the aromatic pairs in these solvents and in isopropanol from previous work (13) is made with a theory which takes into account solvent effects, predicting a dependence of the specific rate constant for an electron transfer on the dielectric properties of the solvent used.

The effects of solvent-solvent interactions on the protonation reactions of the biphenylide radical ion in mixed solvent systems are discussed for the solvent systems ethanol-ethylenediamine, ethanol-
diethylamine, ethanol-triethylamine, ethanol-cyclohexane, ethylene glycol-ethylenediamine, and ethylene glycol-triethylamine. Some data were obtained for the water-ethylenediamine system.

The rate equation for the decay of a radical anion being formed by reaction 2 and decaying by reactions 3 and 4 is given by:

\[-\frac{d[A^-]}{dt} = -k_2[e_{sol}][A] + k_3[RCH_2][A^-] + k_4[RCH][A^-]\] 

where \(k_2\), \(k_3\), and \(k_4\) are the specific rate constants for reactions 2, 3, and 4, respectively.

The formation reaction of the biphenylide ion in ethanol has a specific rate constant of \(k_2 = 4 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}\), as determined by Arai and Dorfman (5) from the decay of the optical absorption of the solvated electron. The half-time for a first-order reaction is given (Appendix) by:

\[\tau = \frac{(\ln 2)}{k} = 0.693/k\] 

where \(k\) is the first-order constant. If the concentration of one of the reactants of a bimolecular reaction remains essentially unchanged relative to the change in concentration of the other reactant, then the reaction is pseudo-first-order, and the first-order constant is the product of the bimolecular rate constant and the concentration of the reactant present in excess. Since the concentration of solvated electrons is in the micromolar range, then at biphenyl concentrations of \(\geq 5 \times 10^{-3}\) M, the anion formation reaction is pseudo-first-order, with a constant

\[k_2' = k_2 [\phi_2] \geq 2 \times 10^7 \text{ sec}^{-1}\] 

Therefore, the half-time is \(\leq 30\) nsec and the formation is essentially complete by the end of the pulse. Since the subsequent decay of the
radical anions has a half-time which ranges from 200 nsec to 2 \(\mu\)sec in this work, the formation does not interfere. The values of \(k_2\) for a number of aromatic compounds appeared (5) to increase with increasing electron affinity and molecular size of the compound used, and these values approached those of rate constants expected for diffusion-controlled reactions. Of the aromatic compounds used in this study, biphenyl has the lowest electron affinity value and is one of the smallest molecules; therefore, it might be expected that the specific rate constants for the formations of the other anions are even greater, i.e., the half-times are shorter for the same concentration of aromatic compound. The total concentration of aromatic compounds used in any experiment of this work was kept > 4 \(\times\) \(10^{-3}\) M with one exception. In diethylamine, the pyrene concentration was 2.5 \(\times\) \(10^{-3}\) M. The large molecular size and high electron affinity of pyrene, relative to biphenyl, combined with the low viscosity of diethylamine relative to ethanol, insures that the formation of the pyrenide ion in diethylamine has a shorter half-time than that of biphenyliide in ethanol. Experimentally, no evidence of the formation reaction after the pulse was seen in the time scale of the observations.

The specific rate constant for the recombination of biphenyliide with its counter-ion in ethanol, \(\text{EtOH}_2^+\), was found (5) to be 3.3 \(\times\) \(10^{10}\) M\(^{-1}\)sec\(^{-1}\). If the recombination reaction were the only mode of decay of the anion and \(\text{EtOH}_2^+\), and if the initial concentrations of the two species are approximately equal, then the decay would appear to be second-order in the anion. The half-time for a second-order reaction is given (Appendix) by:

\[
\tau_{1/2} = \frac{1}{(k_3[\text{EtOH}_2])_0} \tag{VI}
\]
where $[\phi^+_2]_0$ is the initial concentration of the anion, which was kept at a few micromolar by low electron pulse intensities used for this study. The half-time, then, for this reaction is $\approx 30 \mu\text{sec}$. This is long relative to the half-times of the reactions of this study, which are generally less than 1 to 2 microseconds. Thus, contributions of this second-order decay to the kinetics of the systems studied were small, and were neglected in most cases. Where this was not possible, its contribution is discussed in the appropriate section.

Under the conditions of sufficiently high concentrations of aromatic compounds and sufficiently low pulse intensities, then, the terms in $k_2$ and $k_3$ of equation III can be neglected, so that:

$$- \frac{d[A^-]}{dt} = k_4[\text{ROH}][A^-]$$

Specific rate constants were determined for the protonation reactions of a number of aromatic radical anions in methanol, ethanol, n-propanol, and isopropanol. A direct correlation was shown to exist between these rate constants and the acidities of the alcohols. This correlation lends support to the interpretation of the first-order decay of the radical anion as a proton transfer from the alcohol:

$$A^- + \text{ROH} \rightarrow \text{AH}^- + \text{RO}^-$$

**ELECTRON TRANSFER REACTIONS**

If a second aromatic compound is present in the system such that its concentration, relative to that of $A_1$, is low enough that $k_2[A_1] >> k_2'[A_2]$, where $k_2$ and $k_2'$ are the specific rate constants for the formation of $A_1^-$ and $A_2^-$, respectively, then essentially only $A_1^-$ will be
formed by electron attachment, and the electron transfer to the second aromatic can be followed:

\[ A_1^- + A_2 \xrightleftharpoons[k_r]{k_f} A_1 + A_2^- \]  

(5)

In the alcohols, under the conditions of low pulse intensity and sufficiently high concentration of aromatic compounds, the rate equation for \( A_1^- \) is closely approximated by

\[- \frac{d[A_1^-]}{dt} = k_f[ROH][A_1^-] + k_f[A_2][A_1^-] - k_r[A_1][A_2^-] \]  

(VIII)

where \( k_f \) and \( k_r \) are the specific rate constants for the forward and reverse reactions, respectively, of Reaction 5 above.

Values for these rate constants for a number of pairs of aromatic compounds were determined in isopropanol (12, 13). That the reaction was occurring as written was supported by the fact that the reaction rate depended in a linear fashion on the concentration of second arene present, and in those cases where a rate constant for the reverse reaction was obtained the values for \( k_f/k_r \) compared very favorably (13) with the values for the equilibrium constants as determined from potentiometric measurements of the reduction potential differences for the appropriate pair in tetrahydrofuran (29). In those few cases where the formation of \( A_2^- \) could be monitored as the reaction progressed, the kinetics of the formation of \( A_2^- \) were reported (12) to be in fairly close agreement with the decay kinetics of \( A_1^- \). This observation further supports the interpretation of the reaction as the electron transfer, as written.

There are simplifying considerations in many cases in the use of Equation VIII. When the equilibrium is overwhelmingly to the right in Reaction 5, i.e., when \( k_f \gg k_r \), which is the case for large differ-
ences in the reduction potentials of the aromatic compounds in the pair, then the term in \( k_r \) can be neglected. Since the condition \([A_2] \gg [A_1^-]\) is always satisfied experimentally, the decay of \( A_1^- \) is pseudo-first-order:

\[
-\frac{d[A_1^-]}{dt} = (k_f[ROH] + k_r[A_2]) [A_1^-] \tag{IX}
\]

and (Appendix):

\[
-ln D_t = (k_f[ROH] + k_r[A_2]) t + C \tag{X}
\]

where \( D_t \) is optical density of \( A_1^- \) at time \( t \), and \( C = -ln D_0 \). A plot of \(-ln D_t\) against time will be linear, with a slope

\[
S = (k_f[ROH] + k_r[A_2]). \tag{XI}
\]

If this slope is determined for a number of concentrations of \( A_2 \), a plot of \( S \) against \([A_2]\) will have a slope \( k_f \) and an intercept \( k_f[ROH] \). If the protonation of \( A_2^- \) by the alcohol is fast relative to the reverse rate of Reaction 5, then again the term in \( k_r \) can be neglected in Equation VIII and the treatment is the same.

In those cases where the rate of protonation of \( A_1^- \) is slow relative to the forward rate of Reaction 5, then the rate equation is given approximately by:

\[
-\frac{d[A_1^-]}{dt} = k_f[A_2][A_1^-] - k_r[A_1][A_2^-]. \tag{XII}
\]

Considerations of initial and equilibrium conditions lead to the integrated equation (Appendix) of the form:

\[
-ln(D_t - D_{eq}) = (k_f[A_2] + k_r[A_1]) t + C \tag{XIII}
\]

where \( D_{eq} \) is the optical density of \( A_1^- \) at equilibrium, and \( C \) is a constant. A plot of \(-ln(D_t - D_{eq})\) against time will have a slope \((k_f[A_2] + k_r[A_1])\). A plot of this quantity against \([A_2]\) will be linear with a
slopes $k_f$ and an intercept $k_f[A_1]$.

The general form of Equation VIII is:

$$-\frac{d[A_1^-]}{dt} = k_i[A_1^-] + k_f[A_2^-] - k_f[A_1][A_2^-]$$  \hfill (XIV)

where, for the alcohols as solvents, $k_i = k_f[ROH]$. In ethylenediamine, the natural decay of $A_1^-$ appears to be an impurity reaction, for which $k_i$ is the first-order constant. A similar expression holds for $A_2^-$, where the term in $k_i$ is replaced by one in $k_{ii}$. The two equations can be solved simultaneously and integrated (Appendix), yielding:

$$D_t = C_1 e^{-\alpha t} + C_2 e^{-\beta t}$$  \hfill (XV)

where $D_t$ is optical density of $A_1^-$, and

$$\alpha = \frac{1}{2}(k_i + k_{ii} + k_f[A_2] + k_f[A_1])$$
$$+ \frac{1}{2}\{(k_i + k_{ii} + k_f[A_2] + k_f[A_1])^2$$
$$- 4(k_{ii}k_f[A_2] + k_i k_f[A_1] + k_{ii}^2)\}^{1/2}. \hfill (XVI)

The C's are functions of the $k$'s, $[A_1]$, $[A_2]$, $[A_1^-]_0$, $[A_2^-]_0$, and $\varepsilon_A d$. $\beta$ is the same as $\alpha$ with a minus sign between terms 1 and 2. However,

$$(\alpha + \beta) = (k_i + k_{ii} + k_f[A_2] + k_f[A_1]). \hfill (XVII)$$

A plot, then, of $(\alpha + \beta)$ against $[A_2]$ will be linear with a slope $k_f$. A knowledge of $k_i$, $k_{ii}$, and $[A_1]$ will lead to a value of $k_f$ from the intercept. Equation XV indicates that the optical density change with time depends on two independent exponentials. A plot of $-\ln D_t$ versus time will be linear at long times, with a slope $\beta$. The long-time decay can be extrapolated back, corrected for, and a plot of $-\ln D_t'$, where $D_t'$ is the optical density at short times corrected for the slower decay, against time will be linear with a slope $\alpha$. Examples are given in the appropriate sections. The determination of $k_f$ for the one
reaction studied in diethylamine was more complex, due to the second-
order natural decays of $A_1^-$ and $A_2^-$ (presumably by counter-ion recom-
binations), and the method used is described in that section.

The treatment of the data varies considerably in going from sol-
vent to solvent, more so than in going from pair to pair of aromatic
compounds. For this reason, and since this study is primarily con-
cerned with solvent effects, the electron transfer reactions are dis-
cussed under the headings of solvent used rather than of the indivi-
dual aromatic donor-acceptor pair.

ETHANOL

Specific rate constants in ethanol have been determined in this
work for the electron transfer reactions of the biphenyldie radical
ion, $\phi_2^-$, to naphthalene and of the pyrenide ion to 9,10-dimethyl-
thracene.

For the former pair, the back reaction is probably slow relative
to the protonation of the naphthalenide ion by ethanol at the concen-
trations of biphenyl used, as will be discussed shortly. The rate ex-
pression would then be:

$$-\frac{d[\phi_2^-]}{dt} = (k_4[\text{EtOH}] + k_p[N])[\phi_2^-] \quad (XVIII)$$

where $[N]$ is naphthalene concentration. Integration (Appendix) gives

$$-\ln D_t = (k_4[R\text{OH}] + k_\phi[N])t + C \quad (XIX)$$

where $D_t$ is optical density of $\phi_2^-$ at time $t$. The optical density of
$\phi_2^-$ was monitored at 615 nm., which is a maximum in the absorp-
spectrum of $\phi_2^-$ (5) and at which wavelength the naphthalenide ion does
not absorb appreciably. Figure 7 is a plot of $-\ln D_t$ versus time for a
number of values of $[N]$. The quantities evaluated as the slopes in
Figure 7:-- Plot of $-\log D_T$ versus time for different naphthalene concentrations. $[\phi_2] = 4.7$ nM; $\square$, [N] = 0 mM; $\bigtriangleup$, [N] = 1.8 mM; $\Delta$, [N] = 3.7 mM.
Figure 7 (see Equation XIX) are plotted against naphthalene concentration in Figure 8. The slope of Figure 8 gives:

\[ k_p = (2.0 \pm 0.6) \times 10^8 \text{M}^{-1}\text{sec}^{-1} \]  

(XX)

for the electron transfer from biphenylylde ion to naphthalene in ethanol.

The rate constant for the protonation of the naphthalenide ion by ethanol is not known, but in isopropanol the protonation rate constant is an order of magnitude larger than that of the biphenylylde ion. If this is the case in ethanol, then the rate constant for the pseudo-first-order protonation of the naphthalenide ion in ethanol has a value of approximately $4 \times 10^5$ sec$^{-1}$. Studies in ethylenediamine to be discussed give a value for the ratio of the rate constant for the forward electron transfer to that of the reverse transfer of $k_f/k_r \approx 9$ for the pair biphenyl-naphthalene. In ethanol, then, the rate constant for the reverse reaction is expected to have a value of approximately $2 \times 10^7$ M$^{-1}$sec$^{-1}$. The first-order constant for the back reaction, then, at $[\phi_2] = 4.7 \times 10^{-3}$ M, has a value $k_r[\phi_2] \sim 10^5$ sec$^{-1}$. Thus, the first-order constant for the protonation is $\sim 40$ times larger than that for the reverse electron transfer, and the initial assumption that the protonation reaction is fast relative to the reverse Reaction 5 at these $\phi_2$ concentrations seems reasonable. A more significant support of the assumption is the observation that the first-order plots of Figure 7 are linear, which they would not be if the reverse electron transfer were occurring appreciably.

The decay of the pyrenidc radical ion in the system pyrene-9,10-dimethylanthracene in ethanol was monitored at 490 nm, the peak of the strongest absorption band of the anion, and at which wavelength the
Figure 8:-- Plot of \((k_4[\text{EtOH}] + k_f[N])\) versus naphthalene concentration. \(\bigcirc, \square\) indicate two independent sets of data.
anion of 9,10-dimethylanthracene does not absorb appreciably. At the absorption maximum of the 9,10-dimethylanthracenide ion (~730 nm.), however, the pyrene ion has a weak absorption band. The protonation reactions are sufficiently slow that the general Equation XII can be used. Integration yields:

\[ D_t = C_1 e^{-\alpha t} + C_2 e^{-\beta t} \]  
(XIII)

such that

\[ (\alpha + \beta) = k_2' + k_2'' + k_r[DMA] + k_r[Pyr] \]  
(XXI)

where \( D_t \) is the optical density of the pyrene ion, and \( k_2' \) and \( k_2'' \) are the first-order rate constants for the protonation reactions of the pyrene and 9,10-dimethylanthracenide ions, respectively. [DMA] and [Pyr] are the concentrations of 9,10-dimethylanthracene and pyrene, respectively. Figure 9 is a plot of \(-\ln D_t\) against time, and \(\alpha\) and \(\beta\) are determined as described previously. Figure 10 is a plot of \((\alpha + \beta)\) against [DMA] for [Pyr] = 4.1 \times 10^{-5} M. The slope of Figure 10 gives:

\[ k_r = (2.0 \pm 0.8) \times 10^9 \text{ M}^{-1} \text{sec}^{-1} \]  
(XXII)

for the electron transfer from pyrene ion to 9,10-dimethylanthracene in ethanol.

A value for \(k_r\) obtained from the intercept \((I = 0.644 \mu\text{sec}^{-1})\) of the plot in Figure 10 is not very reliable. Subtracting the contributions to the intercept of the first-order protonation rate constants for the two anions (about 40% of the intercept) gives a rough value of

\[ k_r \sim 9 \times 10^7 \text{ M}^{-1} \text{sec}^{-1} \]  
(XXIII)

for the electron transfer from the 9,10-dimethylanthracenide ion to pyrene in ethanol.
Figure 9: Plot of \(-\ln D_t\), O, versus time and \(-\ln D_t'\), \(\diamond\), versus time for \([\text{Pyr}] = 4.1 \text{ mM}\) and \([\text{DMA}] = 1.3 \text{ mM}\) in ethanol.
Figure 10: Plot of \((\alpha + \beta)\) versus [DMA] for [Pyr] = 4.1mM in ethanol.
ETHYLENEDIAMINE

Specific rate constants in ethylenediamine have been determined in this work for the electron transfer reactions of the anions in the following pairs of aromatic compounds: biphenyl-naphthalene, pyrene-9,10-dimethylantracene, and biphenyl-phenanthrene.

The optical density of the biphenylide radical ion for the biphenyl-naphthalene system was monitored at 600 nm., near the maximum (~617 nm.) of one of the absorption bands of \( \phi^- \). No attempt was made to monitor the formation of the naphthalenide ion at its absorption peak around 810 nm. The natural decay, probably by impurity reaction, of the biphenylide ion in ethylenediamine has a half-time of approximately 13 \( \mu \)sec., as does that of the naphthalenide ion.

The general form of the rate equation was used, which has the integrated form

\[
D_t = C_1 e^{-\alpha t} + C_2 e^{-\beta t} \quad (XIII)
\]

where \( D_t \) is the optical density of \( \phi^- \) and

\[
(\alpha + \beta) = k_1 + k_{11} + k_2[N][\phi^-] + k_3[\phi][N^-] \quad (XXIV)
\]

where \( k_1 \) and \( k_{11} \) are the first-order rate constants for the natural decay of \( \phi^- \) and \( N^- \), respectively. Figure 11 shows the decay in absorption of \( \phi^- \) at different concentrations of naphthalene. As can be seen from the Figure, when \([N] = 0\) the transmitted light decays nearly linearly in the time scale used, so that the corrected optical density at short times, \( D'_t \), can be obtained from the ratio of transmitted light extrapolated from long times to the actual transmitted light. That is,

\[
D'_t = D_t - D_{t,\text{long}} = \log(I_0/I_t) - \log(I_0/I_{t,\text{long}}) = \log(I_{t,\text{long}}/I_t) \quad (XXV)
\]
Figure 11: Rate curves for $\phi_e^-$ at different naphthalene concentrations in ethylenediamine. From top to bottom, $[N] = 0, 0.17, 0.38, \text{ and } 1.06 \text{ mM}$ for the four curves. $[\phi_e] = 9.1 \text{ mM.}$
where $D_t$ is the actual optical density and $D_{t,\text{long}}$ is the correction for the long-time decay. A plot of $-\ln D_t'$ against time for three concentrations of naphthalene are shown in Figure 12. The slopes of these plots give values for $\alpha$. Values for $\beta$ are obtained from the long-time decays ($\beta$ is generally $< 1/3$ of $\alpha$). A plot of $(\alpha + \beta)$ against concentration of naphthalene is given in Figure 13. The different symbols are data points from five independent runs. The sets were normalized to a common intercept because of variations in $k_i$, $k_{11}$, and $[\phi_2]$ from set to set. The slope of Figure 13 gives:

$$k_f = (2.1 \pm 0.4) \times 10^9 \text{ M}^{-1}\text{sec}^{-1} \quad (XXVI)$$

for the electron transfer from biphenylide to naphthalene in ethylenediamine.

The values of $k_i$ and $k_{11}$ for two of the five sets were found to be approximately $0.05 \mu\text{sec}^{-1}$. For these sets, the intercepts of the individual $(\alpha + \beta)$ plots were $I_1 = (1.5 \pm 0.4) \mu\text{sec}^{-1}$ and $I_2 = (2.0 \pm 0.4) \mu\text{sec}^{-1}$, where $[\phi_2]_1 = 6.4 \times 10^{-3}$ M, and $[\phi_2]_2 = 9.1 \times 10^{-3}$ M. Subtracting for the contributions to the intercepts by $k_i$ and $k_{11}$ ($I = k_i + k_{11} + k_f[\phi_2]$), and dividing by $[\phi_2]$ gives:

$$k_r = (2.3 \pm 0.6) \times 10^8 \text{ M}^{-1}\text{sec}^{-1} \quad (XXVII)$$

for the transfer of an electron from the naphthalenide ion to biphenyl in ethylenediamine. Thus, the ratio

$$k_f/k_r \approx 9.1. \quad (XXVIII)$$

This value is slightly higher than the value for the equilibrium constant as determined from the reduction potential difference of the pair of aromatic compounds in tetrahydrofuran, where $K_{eq} = 5.3$. The minimum value determined above within the indicated error limits is
Figure 12: -- Plot of $-\ln D'_T$ versus time for the decay of $\phi_2^-$ in ethylenediamine. $[\phi_2] = 9.1$ mM; $[N] = 0.17$ mM; $[N] = 1.1$ mM; and $[N] = 4.6$ mM.
Figure 13: Plot of $(\alpha + \beta)$ versus concentration of naphthalene for five independent sets of data. The sets are normalized to a common intercept.
If the \((\alpha + \beta)\) method does, in fact, separate \(k_f\) and \(k_r\), then the \(k_f\) calculated from the slope of Figure 13 should not depend on the concentration of biphenyl from set to set. Figure 14, which is a plot of \(k_f\) from the individual data sets of the previous figure against the concentration of \(\phi_2\) for these sets, shows that \(k_f\) is essentially constant over this limited range of \([\phi_2]\).

The optical density of the pyrenide radical ion was monitored at 490 nm., near an absorption maximum in its spectrum. No attempt was made to monitor the formation of the 9,10-dimethylanthracenide ion at its absorption maximum \(\lambda_{\text{max}} \sim 750\) nm.). Figure 15 shows the decay in the absorption of pyrenide ion at different concentrations of dimethylanthracene. The treatment is the same as for the previous pair, and the plot of \((\alpha + \beta)\) against concentration of 9,10-dimethylanthracene is given in Figure 16. The slope gives:

\[
k_f = (4.4 \pm 1.0) \times 10^8 \text{ M}^{-1}\text{sec}^{-1}
\]

for the electron transfer from the pyrenide ion to 9,10-dimethylanthracene in ethylenediamine.

The intercept of Figure 16, less approximately \(4%\) for the contributions of \(k_i\) and \(k_{ii}\), is \(I = (1.0 \pm 0.4) \mu\text{sec}^{-1}\), and division by \([\text{Pyr}]\) gives:

\[
k_r = (2.2 \pm 0.9) \times 10^8 \text{ M}^{-1}\text{sec}^{-1}
\]

for the electron transfer from 9,10-dimethylanthracenide ion to pyrene in ethylenediamine. The value for the ratio of \(k_f\) to \(k_r\), then, is \(\sim 20\), whereas the value of \(K_{\text{eq}}\) from potentiometric data is 30. Within the error limits indicated for \(k_f\) and \(k_r\), however, there is agreement.
Figure 14: -- Plot of $k_f$ for the electron transfer from the biphényldiide ion to naphthalene in ethylenediamine versus $[\varphi_2]$. 
Figure 15: Rate curves for pyrene ion decay at different concentrations of 9,10-dimethylanthracene in ethylenediamine. From top to bottom, [9,10-DMA] = 0, 0.23, and 0.47 mM for the three curves. [Pyrene] = 4.4 mM.
Figure 16:-- Plot of $(\alpha + \beta)$ versus concentration of 9,10-dimethyldimethylanthracene. [Pyrene] = 4.4 mM.
The optical density of the biphenyldiene ion was monitored at 600 nm for the biphenyl-phenanthrene system in ethylenediamine. No attempt was made to monitor the formation of the phenanthreneide ion at its absorption maximum in the near-infrared ($\lambda_{\text{max}} \sim 1100$ nm.). Figure 17 shows the decay in the absorption of $\phi_2^-$ at different concentrations of phenanthrene. The treatment is the same as for the two previous cases and the plot of $(\alpha + \beta)$ against phenanthrene concentration is shown in Figure 18 for two independent sets of data, normalized to a common intercept due to variations in $k_i$, $k_{iii}$, and $[\phi_2]$ between the runs.

$$k_{f} = (4.2 \pm 1.6) \times 10^9 \text{ M}^{-1}\text{sec}^{-1}$$

for the electron transfer from the biphenyldiene ion to phenanthrene. The value for $K_{eq}$ from potentiometric data is $\approx 250$; consequently, the small intercept for these two sets of data reflect the low value of $k_f$. A rough estimate of $k_f$ from the intercepts of the two sets of data gives:

$$k_f \approx 7 \times 10^7 \text{ M}^{-1}\text{sec}^{-1}$$

for the electron transfer from phenanthreneide ion to biphenyl in ethylenediamine.

If there were no natural (impurity) decay of the anions, then in a system where $A_1$ is the donor compound and $A_2$ the acceptor, at equilibrium:

$$-\frac{d[A_1^-]}{dt} = 0 = k_f[A_2][A_1^-]_{eq} - k_r[A_1][A_2^-]_{eq}$$

or

$$k_f/k_r = \frac{[A_1]/[A_2]}{([A_2^-]_{eq}/[A_1^-]_{eq})}$$

Initially, however, $[A_1^-]_0 \gg [A_2^-]_0$ so that $[A_2^-]_{eq} = [A_1^-]_0 - [A_1^-]_{eq}$, and Equation XXXIV becomes:
Figure 17: Rate curves for $\Phi_2^-$ decay in ethylenediamine at different phenanthrene concentrations. From top to bottom, [Phen] = 0, 0.20, and 0.53 mM for the three curves. [$\Phi_2^-'] = 5.4$ mM.
Figure 18:-- Plot of $(\alpha + \beta)$ versus [Phenanthrene] for two independent sets of data. The sets are normalized to a common intercept.
\[ k_f/k_r = \frac{[A_1]/[A_2]}{([A_1^-]_0/[A_1^-]_{eq} - 1)} \]  
(XXXV)

Substitution of D/ed for \([A_1^-]\) gives:

\[ (k_f/k_r) + 1 = \frac{([A_1]/[A_2])(D_0/D_{eq})}{([A_1]/[A_2])(D_0/D_{eq})} \]  
(XXXVI)

For a given ratio of \([A_1]/[A_2]\), an increase in \(D_0/D_{eq}\) in going from pair to pair should reflect an increase in \(k_f/k_r\). Because of the anion decay and the difficulty of obtaining \(D_0\), no calculations have been attempted, but the lower curves of Figures 11, 15, and 17, for which the ratios \([A_1]/[A_2]\) are the same within a factor of 2, show that the ratio \(D_0/D_{eq}\) increases in going from biphenyl-naphthalene to pyrene - 9,10-dimethylantracene, to biphenyl-phenanthrene in ethylenediamine. The ratio \(k_f/k_r\) does, in fact, increase in this order.

**DIETHYLAMINE**

The rate constant for the electron transfer from pyrenide ion to 9,10-dimethylantracene has been determined in diethyamine. The anions of both compounds decay in diethyamine by a second-order process, which is presumably mostly the counter-ion recombination reaction

\[ A^- + S^+ \xrightarrow{k_a} A + S \]  
(6)

where \(S^+\) is the positive charge carrier in diethyamine. The rate equation for the decay of pyrenide in the presence of 9,10-dimethylantracene is given by:

\[-d[Pyr]/dt = k_S[S^+][Pyr^-] + k_f[DMA][Pyr^-] - k_p[Pyr][DMA^-] \]  
(XXXVII)

Since there is a similar expression for \(DMA^-\) and a third equation for \(S^+\), any process of linearization of the data would be difficult, if not impossible. Assume, however, that

\[ [Pyr^-]_0/[DMA^-]_0 = \frac{k_2 [Pyr]\text{'}/[DMA]}{k_2 \text{'}/[DMA]} \]  
(XXXVIII)

where \([Pyr^-]_0\) and \([DMA^-]_0\) are initial concentrations (at the end of the
pulse), and $k_2$ and $k_2'$ are the specific rate constants for the formation reactions of the pyrenide and 9,10dimethylanthracenide ions, respectively, by electron attachment (Reaction 2). This assumption is discussed later. Substitution of $[\text{DMA}^-]_0$ from Equation XXXVIII into Equation XXXVII gives:

$$-(\frac{d[\text{Pyr}^-]}{dt})_0 = k_6[S^+]_0[\text{Pyr}^-]_0 + (k_F - k_2'k_T/k_2)[\text{DMA}][\text{Pyr}^-]_0 \quad (...) (XXXIX)$$

Substituting $D/dt$ for $[\text{Pyr}^-]$ and dividing by $D_0$ gives:

$$-1/D_0(\frac{dD}{dt})_0 = k_6[S^+]_0 + (k_F - k_2'k_T/k_2)[\text{DMA}] \quad (...) (XL)$$

Thus a plot of the left-hand-side of Equation XL against $[\text{DMA}]$ will be linear (if the pulse variation is small so that $[S^+]_0$ is constant) with a slope $(k_F - k_2'k_T/k_2)$.

Figure 19 is a rate curve for the decay of the optical absorption of pyrenide ion at 500 nm, near its absorption maximum in diethylamine. The upper trace shows the emitted light from the solution. For this one solution, the emission lasted long enough that a correction to $I_{tr}$ had to be made for the first 150 nsec or so after the pulse. The upper channel was expanded electronically by a factor of 2 vertically, relative to the bottom channel. A plot of optical density against time is shown in Figure 20. There appears to be a well-defined break in the kinetics, with an initial rapid decay ($\tau_2 \approx 100$ nsec) followed by a much slower decay. This rapid decay has been observed for the biphthalide and pyrenide ions in aniline (20), and was attributed to recombination of geminate ion pairs. No attempt was made in the present work to determine the absolute kinetics of this decay. It is clear from Figure 20 that the formation during the pulse is considerably faster than the slow decay. Then during the pulse
Figure 19:-- Rate curves for the decay of the pyrenide radical ion in diethylamine. [Pyrene] ≈ 3 mM.
Figure 20: -- Plot of optical density versus time for the pyrenide ion in diethylamine, from Figure 19.
and

\[-(d[Pyr^-]/dt)_{\text{pulse}} \approx k_2[Pyr][e^-_{\text{sol}}]\]  \hspace{1cm} (XLI)

\[-(d[DMA^-]/dt)_{\text{pulse}} \approx k'_2[DMA][e^-_{\text{sol}}]\]  \hspace{1cm} (XLII)

The ratio of the two equations should give an approximate measure of the ratio of concentrations of the two anions at the end of the pulse, i.e.,

\[
[Pyr^-]_0/[DMA^-]_0 \approx \frac{k_2[Pyr]}{k'_2[DMA]} \]  \hspace{1cm} (XXXVIII)

which was the initial assumption for the use of this initial slope method. The occurrence, however, of the ultra-fast decay precludes measurements in this system of the initial slopes, that is, slopes of the slower decay at the end of the pulse. Furthermore, there is no simple correction which can be made for the error involved in using slopes at later times, and the effects are serious, since Equation XXXVIII becomes less and less valid at later times, due to the decrease in $[Pyr^-]_t$ and the simultaneous increase in $[DMA^-]_t$ as the electron transfer reaction proceeds. The effects of the back reaction further complicate any determination of the effects of the treatment at $t \neq 0$. The method used was to plot the l.h.s. of Equation XL against $[DMA]$, for which the slopes were approximately linear, and then to empirically plot these slopes as a function of time ($\log S$ vs. $t$). Figure 21 shows plots of $-1/D_T(dD/dt)_T$ against $[DMA]$, where $T = 0.2, 0.3, 0.4, 0.5 \mu\text{sec}$ after the end of the pulse, from top to bottom, respectively. Each point represents the average value from 3, 4, or 5 separate prints. The slopes (from top to bottom) are 1.63, 1.40, 1.20, and 1.08 $\mu\text{M}^{-1}\mu\text{sec}^{-1}$. A plot of $\log$ (slope) against time is shown in Figure 22. The value of the intercept is:

\[I = 10.33 \pm 0.16\]  \hspace{1cm} (XLI)
Figure 21: -- Plot of the left-hand-side of Equation XL versus [9,10-DMA] for: O, \( \tau = 0.2 \mu \text{sec} \); \( \Delta \), \( \tau = 0.3 \mu \text{sec} \); \( \square \), \( \tau = 0.4 \mu \text{sec} \); and \( \Diamond \), \( \tau = 0.5 \mu \text{sec} \) after the end of the pulse.
Figure 22:— Plot of the log of the slopes of Figure 21 versus \( \tau \).
Then

$$(k_f - k_2'k_f/k_2) = (2.1 \pm 1.0) \times 10^{10} \text{M}^{-1}\text{sec}^{-1} \quad (XLIV)$$

As previously discussed, the value of $k_2$ appears (5) to depend on electron affinity and molecular size, but the reaction rate constants have values approaching those expected for diffusion-controlled reactions. Neither the pyrene ion nor the 9,10-dimethylantracenide ion was included in that study, but a crude interpolation based on electron affinities and molecular sizes yields an estimate for $k_2'/k_2$ of approximately 1.3. The ratio is certainly not far from unity since the molecular sizes are probably comparable and the electron affinity difference is small. In going from naphthalene to naphthacene the ratio of $k_2$’s was found (5) to be < 2, in spite of the difference in size and in the electron affinity ($\Delta$E.A. $\approx$ 20 kcal/mole). Using a value of $K_{eq} \approx 30$ as calculated from potentiometric data, and the value of $k_2'/k_2 \approx 1.3$ above, the second term in Equation XLIV is seen to be approximately 4% of the first term, and:

$$k_f = (2.2 \pm 1.0) \times 10^{10} \text{M}^{-1}\text{sec}^{-1} \quad (XLV)$$

for the electron transfer from the pyrene ion to 9,10-dimethylantracene in diethylamine.

As a check on this method, data previously analyzed for the pair biphenyl-naphthalene in ethylenediamine was treated exactly similarly. The linearization of slopes with $\tau$ was best accomplished in this case by a log-log plot, where $\tau = 1$ was defined as the end of the pulse. The plot of the slopes against $\tau$ is shown in Figure 23. The intercept was determined to be $I = 2.0 \times 10^9 \text{M}^{-1}\text{sec}^{-1}$. The value for $k_2'/k_2$ is (5) $\approx 1.3$, and $k_f/k_r \approx 9$; thus:
Figure 23: -- Plot of the log of the slopes versus $\tau$ for the case of electron transfer from $\phi_2^-$ to naphthalene in ethylenediamine.
\[ k_F = 2.3 \times 10^9 \, \text{M}^{-1}\text{sec}^{-1} \]  

which compares very well with the previously determined value of \( 2.2 \times 10^9 \, \text{M}^{-1}\text{sec}^{-1} \) for this data.

In order to provide a test, not only for this value of \( k_F \), but also for the proposed decay mechanism of the pyrene ion, a program was set up for the analog computer which provided for the forward and reverse electron transfers, and for the two second-order recombination reactions of the anions. This program is shown schematically in Figure 24. Employed were: three integrating amplifiers, one each for the two anions and the counter-ion; two multipliers for the second-order reactions; a number of inverting amplifiers for sign changes; and four potentiometers representing the rate constants \( k_a, k_a', k_r' \) and \( k_r' \), where \( k_r' = k_f[\text{DMA}] \) and \( k_r' = k_r[\text{Pyr}] \). The greatest problem with such a program for these studies is the requirement that the initial concentrations of the species be known. It was assumed for this purpose that \( [\text{Pyr}^-]_0 \gg [\text{DMA}^-]_0 \) and \( [S^+]_0 \approx [\text{Pyr}^-]_0 + [\text{DMA}^-]_0 \), so that essentially \( [\text{DMA}^-]_0 \approx 0 \) and \( [S^+]_0 \approx [\text{Pyr}^-]_0 \). It was also assumed that the extinction coefficient at \( \lambda_{\text{max}} \) of the pyrene anion was essentially independent of solvent, and the value of \( e_{\text{Pyr}^-}^{480} = 4.95 \times 10^4 \, \text{M}^{-1}\text{cm}^{-1} \) reported for pyrene in tetrahydrofuran (7) was used. The values of \( k_a \) and \( k_a' \) were determined from the second-order decay curves of the individual anions in diethylamine. Second-order plots are shown in Figure 25. The above extinction coefficient and that reported (7) for 9,10-dimethylanthracenide ion in tetrahydrofuran were used to calculate \( k_a \) and \( k_a' \):

\[ k_a = 1 \times 10^{12} \, \text{M}^{-1}\text{sec}^{-1} \]  

(XLVII)
Figure 2: -- Schematic of the analog computer program for the pyrene-9,10-dimethylantracene system in diethylamine.
Figure 25: Second-order plots for the decays of pyrenide (□) and 9,10-dimethylanthracene−(○) in diethylamine.
for pyrene ion; and

$$k_{o}^{'} = 6.3 \times 10^{11} \text{ M}^{-1}\text{sec}^{-1}$$  \hspace{1cm} \text{(XLVIII)}

for dimethylanthracenide. As previously indicated, the value of $k_{o}$ for \( \phi_{2}^- \) in ethanol is \( 3.3 \times 10^{10} \text{ M}^{-1}\text{sec}^{-1} \), which is 20 to 30 times less than these values in diethylamine. Apparently the 3-fold decrease in viscosity and the ten-fold decrease in dielectric constant in going from ethanol to diethylamine have a fairly large effect, as expected from theory (31). The values of $k_{o}$ for biphenylide and pyrene in tetrahydrofuran were determined from the second-order plots of Figure 26 to be \( 3.0 \times 10^{11} \text{ M}^{-1}\text{sec}^{-1} \) and \( 3.5 \times 10^{11} \text{ M}^{-1}\text{sec}^{-1} \), respectively, based on the reported (7, 32) extinction coefficients. Furthermore, the rate curves for the second-order decays of the two anions of pyrene and 9,10-dimethylanthracene were reproduced by the analog computer using these extinction coefficients and values for $k_{o}$ and $k_{o}^{'}$ of \( 1.4 \times 10^{12} \text{ M}^{-1}\text{sec}^{-1} \) and \( 6.5 \times 10^{11} \text{ M}^{-1}\text{sec}^{-1} \) respectively, in good agreement with the values from the linearization. With these numbers, then, and with the initial concentration of pyrene ion set at approximately \( 3 \times 10^{-7} \text{ M} \), plots were made from the computer outputs of concentration versus time using values of $k_{f}^{'}$ and $k_{f}^{'}$ for four different values of dimethylanthracene concentration. In all cases, the analog computer curve fits were best for values of $k_{f}^{'}$ within \( \pm 25\% \) of the value calculated by the initial slope method. The first and last of the four curves (with lowest and highest concentration of 9,10-dimethylanthracene, respectively) are shown in Figure 27. The circles are experimental points; the solid lines are those for the analog computer plot; and the dashed lines are computer plots for \( \pm 25\% \) of the best fit value for $k_{f}^{'}$. These fits provide
Figure 26: Second-order plots for the decay of pyrenide (□) and the decay of biphenylide (○) in tetrahydrofuran.
Figure 27:-- Experimental points ( ⭕) and analog computer plots for the decay of pyrenide ion in the system pyrene-9,10-dimethylanthracene in diethylamine.
support not only for the value of $k_\tau$, but for the proposed mechanism for the decay of the pyrenide ion in diethylamine.

**SUMMARY AND CORRELATION WITH THEORY**

Table 1 lists the experimentally determined values for $k_\beta$ (either $k_\tau$ or $k_\beta$) from this work and earlier work in isopropanol (13).

**TABLE 1**

**EXPERIMENTAL RATE CONSTANTS FOR ELECTRON TRANSFER REACTIONS**

<table>
<thead>
<tr>
<th>Donor-Acceptor Pair</th>
<th>$k_\beta \times 10^{-9}$ (M$^{-1}$sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EtOH</td>
</tr>
<tr>
<td>DMA$^-$, PYR</td>
<td>0.09</td>
</tr>
<tr>
<td>NAPH$^-$, $\phi_2$</td>
<td>-</td>
</tr>
<tr>
<td>$\phi_2^-$, NAPH</td>
<td>0.19</td>
</tr>
<tr>
<td>PYR$^-$, DMA</td>
<td>2.0</td>
</tr>
<tr>
<td>$\phi_2^-$, PHEN</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$These data are from Reference 13.

The values for the 9,10-dimethylanthracenide-pyrene and the naphthalenide-biphenyl pairs, the first two pairs in the table, were determined as back reactions as described. It is seen that in going from ethanol to ethylenediamine, and to diethylamine in the case of pyrenide-9,10-dimethylanthracene; which is the order of decreasing dielectric constants of the solvents, there is a general increase in the rate constants, in some cases by an order of magnitude.

These data can be used to test the validity of a theory developed by Marcus (14-21) for electron transfer reactions. In this model, the
rate constant for a simple electron transfer is given by:

\[ k_{\text{act}} = Z e^{-\Delta F^*/RT} \]  

where \( \Delta F^* \) is the free energy of activation. \( Z \) is the collision number, which has been taken by Marcus to be about \( 10^{11} \text{ M}^{-1}\text{sec}^{-1} \), equivalent to the collision number in the gas phase, and hence independent of solvent properties. \( \Delta F^* \) is given by:

\[ \Delta F^* = \omega + \frac{\lambda}{4} + \frac{\Delta F^0}{2} + \frac{(\Delta F^0)^2}{4\lambda} \]  

where \( \omega \) is the difference in work in bringing the reactants together and separating the products. When one reactant is uncharged, the coulombic attraction depends only on the induced dipole effect and is small, and \( \omega \) is neglected. \( \Delta F^0 \) is the standard free energy of reaction, which is taken as the difference in reduction potentials for the neutral aromatic compounds in the donor-acceptor pair. \( \lambda \) is a parameter to account for the necessity of reorganization of the solvent in forming the activated complex from the neutral molecule and the solvated anion, and is given (neglecting a term for reorganization of bond angles and lengths, which is presumed small for the aromatics) by:

\[ \lambda = \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \left( \frac{1}{D_{\text{op}}} - \frac{1}{D_s} \right) (\Delta e)^2 \]  

The effective radii of the reactants, \( a_1 \) and \( a_2 \), may include a dielectrically saturated monolayer of solvent around the anion. The encounter radius \( r \) is taken to be \( (a_1 + a_2) \). The optical dielectric constant, \( D_{\text{op}} \), is the square of the refractive index, and \( D_s \) is the static dielectric constant. \( \Delta e \) is the change in charge of the donor, which for this case is +1.
The theory is developed on the premise that there is little overlap of electronic orbitals of the reacting species in the activated complex (14) for a simple electron transfer. Two states are considered to make up the activated complex, both having the same atomic (including solvent) configuration, but one having the electronic configuration of the reactants and the other having the electronic configuration of the products. This arises from considerations requiring the energies of the two states to be equal (14). Consequently, there must be an appropriate fluctuation of solvent molecules to attain the proper atomic configuration before the activated complex is formed. The parameter, λ, of the theory, which accounts for this solvent reorganization, arises from considerations of two types of polarization of the medium: an equilibrium polarization, i.e., one which can "follow" the actual electronic transition; and a non-equilibrium polarization (determined by the permanent dipole character of the solvent) which cannot follow the transition.

For a meaningful correlation with theory, the experimental value of $k_{\text{act}}$ must be extracted from $k_5$ through the relation (19):

$$k_5^{-1} = k_{\text{act}}^{-1} + k_{\text{diff}}^{-1}$$  \hspace{1cm} (LII)

where $k_{\text{diff}}$ is the diffusion-controlled rate constant.

The dependence of $k_{\text{act}}$ on the reduction potential difference as predicted by the theory was tested in isopropanol (13) for eight donor-acceptor pairs. The values of $k_5$ for two of these were determined as back reactions. For this correlation, $a_1$ was taken as $a_1 \approx a_2 \approx 5\text{Å}$ for all molecules, which came from considerations of molecular dimensions, and hence $r \approx 10\text{Å}$. This gave a value for the reorganization parameter.
of $\lambda = 16$ kcal/mole. $\omega$ was neglected. From the data of that work, values of $k_5,_{\text{act}}$ have been calculated from Equation LII, using $5.7 \times 10^9$ M$^{-1}$sec$^{-1}$, the average of $k_5$ for the two pairs having the largest reduction potential difference, as $k_{\text{diff}}$. Table 2 lists the donor-acceptor pairs, the reduction potential differences, values of $k_5$ from Reference 13, values of $k_5,_{\text{act}}$, and the correlation between the experimental and calculated $k$'s, normalized to the biphenylide-naphthalene pair. This assumes that the collision number is the same for all pairs and therefore cancels out.

**TABLE 2**

VALUES OF $k_5$ IN ISOPROPANOL AND CORRELATION WITH THEORY

<table>
<thead>
<tr>
<th>Donor-Acceptor Pair</th>
<th>$k_5 \times 10^{-8}$</th>
<th>$\Delta F^0$</th>
<th>$k_{\text{act}} \times 10^{-8}$</th>
<th>$k_{\text{act}}$</th>
<th>$k_{\text{calc}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANTHR$^-$, PYR</td>
<td>0.21$^a$</td>
<td>+2.61</td>
<td>0.21</td>
<td>0.081</td>
<td>0.041</td>
</tr>
<tr>
<td>DMA$^-$, PYR</td>
<td>0.37$^a$</td>
<td>+2.01</td>
<td>0.37</td>
<td>0.14</td>
<td>0.074</td>
</tr>
<tr>
<td>$\phi_2^-$, N</td>
<td>2.6$^a$</td>
<td>-0.99</td>
<td>2.7</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$\phi_2^-$, PHEN</td>
<td>6$^a$</td>
<td>-3.28</td>
<td>6.7</td>
<td>2.6</td>
<td>5.3</td>
</tr>
<tr>
<td>PYR$^-$, DMA</td>
<td>13$^a$</td>
<td>-2.01</td>
<td>17</td>
<td>6.5</td>
<td>2.2</td>
</tr>
<tr>
<td>PYR$^-$, ANTHR</td>
<td>18$^a$</td>
<td>-2.61</td>
<td>26</td>
<td>10.1</td>
<td>3.4</td>
</tr>
<tr>
<td>$\phi_2^-$, PYR</td>
<td>50$^a$</td>
<td>-12.2</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\phi_2^-$, ANTHR</td>
<td>64$^a$</td>
<td>-14.8</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ These data are from Reference 13.

Examination of the last two columns, which include rate constants ranging
over two orders of magnitude, shows a fairly good semi-quantitative
correlation between experiment and theory on this relative basis.
Since only one solvent was used, the parameter $\lambda$ was a constant rather
than a variable, and hence the dependence of $k_5$ on solvent properties
was limited to this one solvent, namely, isopropanol.

Table 1 qualitatively shows this same trend of increasing rate
constants in ethanol and ethylenediamine in going down the pairs, which
is the order of increasing reduction potential differences of the pairs.
In addition, the general increase in going through the solvent series
from ethanol to diethylamine is expected on the basis of the dependence
of the rate constant on the solvent reorganization parameter $\lambda$ pre-
dicted by the theory, since for the four solvents ethanol, isopropanol,
ethylenediamine, and diethylamine, the values of $\lambda$ (assuming the same
values of $a_1 \approx a_2 \approx 5\text{Å}$ as in isopropanol) are 16.6, 15.8, 13.5, and 8.0
kcal/mole, respectively. Assuming the value of $k_{\text{diff}} = 5.7 \times 10^9 \text{M}^{-1}\text{sec}^{-1}$
in isopropanol, and correcting for viscosity differences between sol-
vents (31), the values of $k_{5,\text{act}}$ were calculated from the values in
Table 1 with Equation LII for the pair pyrene-9,10-dimethylnaphthalene
in the four solvents. Figure 28 is a plot of $\log k_{5,\text{act}}$ versus $\lambda$ for
this pair. The solid line was calculated from the theory. Since the
correlation depends on the change in $k_{5,\text{act}}$ with $\lambda$, the theoretical (so-
lid) line has been shifted upwards approximately 0.5 log units, or a
factor of 3 in the absolute values of the rate constants. It is clear
that $k_{5,\text{act}}$ increases in the direction predicted by the theory, and, for
this limited series, the data again support the model on a semi-quantitative basis.
Figure 28: Plot of $\log k_{5,act}$ from experimental values given in Table 1 versus $\lambda$. The solid line is calculated from theory.
PROTON TRANSFER REACTIONS

For the protonation reaction of the biphenylide ion in the simple alcohols:

\[ \phi_2^- + \text{ROH} \rightarrow \phi_2\text{H}^+ + \text{RO}^- \]  

the rate equation for the decay of \( \phi_2^- \) is given by:

\[ -\frac{d[\phi_2^-]}{dt} = k_4[\text{ROH}] [\phi_2^-] = k_4' [\phi_2^-] \]  

where \( k_4' \) is the pseudo-first-order constant. As previously discussed, the experimental conditions of this work are such that contributions by the formation of \( \phi_2^- \) and by its decay by counter-ion recombination to the rate equation are small. The value of \( k_4' \) should, barring solvent effects, be a linear function of the alcohol concentration. However, solvents effects are seen to have a considerable bearing on the value of \( k_4' \) for the biphenylide ion in mixed solvent systems involving ethanol or ethylene glycol as the proton donor. The value of \( k_4' \) has been determined as a function of composition for a number of mixed-solvent systems, the major ones of which are discussed individually below. The results are then summarized and discussed in a general way. The kinetics of the decay of \( \phi_2^- \) were monitored at 600nm.

ETHANOL-ETHYLENEDIAMINE

As was seen from the upper rate curve of Figure 11, the decay of \( \phi_2^- \) is very slow in ethylenediamine in the microsecond time scale. Its decay in ethanol, on the other hand, has a half-time of \( \sim 1.2 \mu \text{sec} \). Figure 29 is a plot of \( k_4' \) against composition of the solvent system ethanol-ethylenediamine. The rate of decay of \( \phi_2^- \) at 60% ethanol is essentially the same as that in ethylenediamine alone; the protonation
Figure 29: -- Plot of the first-order decay constant for $\phi_e^-$ versus composition in the ethanol-ethylenediamine solvent system. Different symbols indicate different 'runs'.
reaction appears to be completely inhibited. The value of $k_4'$ then rises to a maximum at $\sim 99.5\%$ ethanol. The inhibition is interpreted as being due to the forming of hydrogen bonds between the amine and the alcohol. The negative heats of mixing for this system indicate association stronger than in the pure alcohol. Thus, the protons of ethanol become considerably less available for reaction with $\phi_2^-$ than they are in ethanol alone. This is not inconsistent, in fact, with the observation of a maximum in the plot of Figure 29, since the presence of the amine-alcohol complex could cause a breaking up of the hydrogen-bonded structure of dimers, trimers and polymers making up the pure alcohol. Inert solvents such as cyclohexane are seen to cause an increase in $k_4'$, as will be described. Negative heats of mixing for ethanol-water systems are generally explained (33) in terms of preferential hydrogen bonding between alcohol and water, and the existence of well-defined complexes has been claimed on the basis of the marked composition dependence of ultrasound absorption (34). Yet, when water is added to alcohols such as t-butanol, the heats of mixing are positive at the alcohol rich end (33), and the results are interpreted in terms of the depolymerization of the alcohol, much like the effects of addition of inert solvents. Such effects would then lead to an increase in the number of "free" OH groups available, in this case for the proton transfer to $\phi_2^-$.  

Quantitative aspects of the complex formation will be discussed in the summary.
ETHANOL-CYCLOHEXANE

The absorption at 600 nm of a pulse radiolyzed solution of biphenyl in cyclohexane is due in part to the cation of biphenyl (35). However, addition of ~0.3 mole percent ethanol eliminates this absorption, as determined in the presence of oxygen, which, as a good electron scavenger, eliminates the anion absorption. Also, indications of the initial rapid decay of $\Phi_2^-$ reported (35) in cyclohexane were observed in this work, but no attempt was made to determine the kinetics of this decay. The yields of $\Phi_2^-$ are approximately 5 times lower in cyclohexane than for ethanol, for a given pulse. This makes the determination of the reaction order more difficult, but a plot of log D against time is fairly linear. Figure 30 is a series of plots of $-\ln D_t$ against time for 0, ~25, ~50, and 100 mole percent ethanol in cyclohexane, from top to bottom, respectively. The slopes of such plots are plotted as a function of composition of solvent in Figure 31. There is an increase in $k_4'$ of approximately 15% in going from alcohol alone to 80% alcohol, and then $k_4'$ stays approximately constant down to the cyclohexane-rich end. This is qualitatively consistent with the observation in ethylenediamine that $k_4'$ increases upon addition of a second solvent. It is also consistent with the "loosening" of protons generally suggested as responsible for the positive heats of mixing observed for this and similar systems, with the O-H stretching frequency shifts in infrared studies (36), and with the recent interpretation (37) of changes in chemical shifts in NMR studies of the hydroxyl protons in ethanol-cyclohexane mixtures as being due to the existence of an equilibrium system of monomers, dimers, and polymers of EtOH units connected by hydrogen bonding. With addition
Figure 30: -- First-order decay plots for $\phi_2$ for 0, ~25, ~50, and 100 mole percent ethanol in cyclohexane, from top to bottom, respectively.
Figure 31: Plot of the first-order decay constant for $\Phi_2^-$ versus composition in the ethanol-cyclohexane solvent system. Different symbols indicate different runs.
of cyclohexane, structure breakdown occurs, with an increase in proton availability, and hence an increase in the "effective" concentration of ethanol for protonation purposes in the mixture over that in the alcohol.

The possibility also exists of a contribution to \( k_4 \) of a solvent reorganization term to account for the necessity of reorganization of the solvent from the aromatic anion to \( \text{EtO}^- \). The theory developed by Marcus has been extended recently, on a conjectural basis, to include atom, and particularly proton transfer reactions (38,39,40). The term for reorganization is not so clearly defined as for the electron transfers; the assumption of little orbital overlap is less valid for an atom transfer, and the transition from one anion to the other is no longer the abrupt change of a simple electronic transition. The direction of change in \( k_4 \) predicted by the theory for the change in dielectric properties of the solvent system would be, in fact, an increase with increasing concentration of cyclohexane, as is observed for \( k_4' \). However, the correlation of the protonation rate constants with acidities (5) indicates that the protonic character of the alcohol seems to be a more dominating factor, since a dependence on dielectric constant would predict a decrease in \( k_4 \) in going from methanol through the solvent series to isopropanol. The contribution of an effect of solvent properties may be masked in the correlation, however, and the rate constants do decrease more slowly than the decreasing acidities. Whether a linear correlation is expected for this comparison of rate constants and acidities is uncertain, as has been discussed (5), but the order of decreasing values for \( k_4 \) with decreasing dielectric constants and increasing acidities still implies that the protonic character of the alcohol is a
predominant factor in determining the rate of protonation.

Although there may well be contributions by a necessity for solvent reorganization, and perhaps by preferential solvation by the alcohol, the evidence for the breaking down of the hydrogen-bonded structure of the alcohol by cyclohexane indicates that the interpretation of the results in terms of a higher "effective" ethanol concentration in the mixture is probably correct.

ETHANOL-TRIETHYLAMINE AND ETHANOL-DIETHYLAMINE

The treatment of the data is essentially the same as in the previous cases. The yields of $\phi_2^-$ at the amine end of the composition curve are again low, but again a plot of $-\ln D_t$ against time is approximately linear. The slopes of the first-order plots are plotted against composition in Figure 32. The break in the curve occurs at $\sim 50\%$ ethanol, but is not nearly so well defined as in the ethylenediamine case, due to the residual decay of $\phi_2^-$ in pure triethylamine. The structure breaking effect is more marked at the alcohol-rich end of the composition curve than for the ethanol-ethylenediamine case, and the maximum is shifted somewhat to lower alcohol concentrations. This may be due to the greater hydrocarbon nature of the amine in this case. The value of the effective ethanol concentration at the maximum is apparently higher than for a cyclohexane-ethanol mixture of similar composition. This may depend on the size of the complex formed between ethanol and triethylamine being an important parameter in the structure breaking, but there are apparently other factors, since for the ethanol-diethylamine case (Figure 33) the effect is larger than for ethanol-triethyl-
Figure 32: -- Plot of the first-order decay constant for $\phi_2^-$ versus composition in the ethanol-triethylamine solvent system.
Figure 33: Plot of the first-order decay constant for $\phi_2^-$ versus composition in the ethanol-diethylamine solvent system.
amine, while the complex should be smaller. Again, there may be additional solvation effects affecting this maximum. The strength of the Et$_3$N-HOEt hydrogen bond has been reported (41) to be $\sim 7.6$ kcal/mole, from infrared studies of the O-H stretching band in the vapor phase (although other workers (42) report values of approximately 5 kcal/mole). This is somewhat stronger than the bond in pure ethanol, reported (43) to be $\sim 4$ kcal/mole. These data are generally consistent with the interpretation of experimental results in terms of the amine-alcohol complex, which itself can break down the hydrogen-bonded EtOH structure, enhancing the protonation.

**ETHYLENE GLYCOL-ETHYLENEDIAMINE**

The behavior of $\Phi_2^-$ in this solvent system is, for the most part, similar to its behavior in ethanol-ethylenediamine, with three exceptions. Firstly, the protonation in ethylene glycol is 2.5 times faster than in ethanol, in accord with the reported (27) rate constant. Secondly, the break in the composition curve seems to occur at $\sim 50\%$ alcohol, whereas in ethanol-ethylenediamine the break appears to be at $\sim 65\%$. The significance of this break in the curve will be discussed in the summary. Thirdly, a break in the kinetics begins to appear at a few percent ethylenediamine in the glycol and does not disappear until the composition is $50\%$ amine. The initial ultra-fast decay ($1/2 = 100$ nanoseconds at its point of maximum effect) at 85% glycol accounts for as much as 60% of the total decay. A rate curve illustrating this is shown on Figure 34. No interpretation of this phenomenon is attempted in the present study, but further research appears to
Figure 34:-- Rate curve for the decay of $\phi_2^-$ in the solvent system of 87% ethylene glycol and 13% ethylenediamine.
be warranted. The first-order constant for the slower decay is plotted versus composition in Figure 35.

ETHYLENE GLYCOL-TRIETHYLAMINE

The pseudo-first-order constant for the decay of $\phi_2^-$ in this system is plotted as a function of composition in Figure 36. The results are striking: there is an 8-fold increase in the rate constant in going from glycol alone to 10% triethylamine. Chemical shifts due to hydrogen bonding have been reported (43) from NMR studies to be smaller in the diols than in ethanol, and this result was interpreted in terms of the existence of a considerable number of intramolecular H-bonds and some "free" OH groups. The results in the present case can be interpreted in terms of the breaking down of the intermolecularly hydrogen bonded structure by the glycol-amine complex, which may force a larger degree of intramolecular bonding, and hence a "loosening" of a proton:

![Diagram showing molecular structure]

Although Pimentel reports (44) that there appears to be no indication of this type of loosening of protons, it has been reported recently (45) that infrared studies have shown that when an $O-H\cdots O$ hydrogen bond is formed the donor hydroxy group oxygen becomes more basic and any hydrogen attached to the acceptor oxygen becomes more acidic. Again, there may well be contributions by solvation effects.

WATER-ETHYLENEDIAMINE

The solubility of biphenyl in water limited the study to that part
Figure 35: -- Plot of the first-order decay constant for $\phi_2^-$ versus composition in the ethylene glycol-ethylenediamine solvent system.
Figure 36:-- Plot of the first-order decay constant for $\phi_2^-$ versus composition in the ethylene glycol-triethylamine solvent system.
of the composition curve shown in Figure 37. It is seen that if protonation of $\Phi_2^-$ is occurring at the water-rich end of the composition curve, its first-order rate constant is nearly three orders of magnitude less than that for ethanol in ethylenediamine. Polarographic studies (46) showed that the protonation of the naphthalenide and the anthracenide ions by water was much slower than by organic proton donors, including methanol, and that there was a significant dependence on the nature of the nonaqueous component in the solvent system.

SUMMARY

This study points out the usefulness of the protonation reactions of the aromatic radical anions as a probe into the complexities of hydrogen-bonding systems. The vast majority of work on systems involving hydrogen-bonding has been concerned with physical properties such as freezing and boiling points, viscosity, and positive and negative deviations from Raoult's Law, although the latter are also affected by differences in internal pressure, polarity, molecular sizes, and hydrogen bonding in the vapor phase. Azeotropic data (47,48) correlate in some cases with the interpretations in the present study. For example, ethylenediamine (b.p. 117°C) and 2-methoxyethanol (b.p. 125°C) form an azeotrope at $\sim 2:1$ alcohol to amine, with b.p. 130°C, which might indicate the formation of a 2:1 complex. Ethylenediamine-butyl alcohol shows similar behavior, also at 2:1, but isobutyl alcohol and the diamine form an azeotrope at $\sim 1:1$; stereochemical factors may be important. Infrared studies (49) on triethylamine-phenol (one of the few infrared studies of two interacting components) indicate formation of a 1:1 complex. Studies of heats of mixing and molar volumes (50) indicate
Figure 37: -- Plot of the first-order decay constant for $\phi_2^-$ versus composition in the water-ethylenediamine solvent system.
formation of a 1:1 complex of isopropanol and isopropylamine. Results of studies of dielectric constant variations with composition of binary mixtures (51) were explained in terms of the formation of a distinct 1:1 complex between o-cresol and cyclohexylamine. The freezing point curve of ethylenediamine-phenol has a maximum at $\sim 67\%$ phenol (52), indicating formation of a 2:1 complex. The "energy of viscous flow" for the ethylene glycol-triethylamine system, when plotted versus composition, gave a curve (53) which was linear up to 30\% glycol (although data points were scarce), and this was interpreted in terms of the formation of a 1:2 glycol-amine complex.

In the present study, the breaks in the curves of $k_4$ versus composition for the systems ethanol-ethylenediamine and ethylene glycol-ethylenediamine give some evidence for the formation of distinct complexes, 2:1 in the former case and 1:1 in the latter, as would be expected. The ordinates of Figures 29 and 34 are expanded ten times and plotted as a function of composition in Figure 38. The break occurs for the ethanol-diamine system at $\sim 65\%$ and for the glycol-diamine system at $\sim 50\%$, which might be interpreted as due to the formation of well-defined complexes, 2:1 ethanol to ethylenediamine and 1:1 glycol to ethylenediamine. This primitive approach, then, of relating the microscopic factors involved with the protonation reaction to the macroscopic properties of the system seems to be reasonably consistent for these mixed solvent systems, as it was for the electron transfer study.

There are other complexities involved in this work. The possibility that the back reaction of the equilibrium

$$\phi_2^- + \text{EtOH} \rightleftharpoons \phi_2\text{H}^- + \text{EtO}^-$$

(8)
Figure 38: -- Data from Figures 29 and 34 plotted on a ten times expanded vertical scale, for the systems ethanol-ethylene-diamine (O) and ethylene glycol-ethylenediamine (Δ).
may be important under the conditions of relatively high values of ethoxide concentration is indicated by the result that the decay of $\phi_2^-$ in a 0.01 M solution of potassium in ethanol has a half-time which is nearly twice that in pure ethanol. The decay is of first-order, however, and there may be complications on the solvent structure by the presence of the metal ion in solution. It might be expected that in the amine-alcohol systems, the equilibrium

$$\text{RNH}_2 + \text{EtOH} \rightleftharpoons \text{RNH}_3^+ + \text{EtO}^-$$

may be contributing through the formation of the ethoxide ion to the back reaction of the equilibrium Reaction 8. Conductivity studies showed, however, that in the water-ethylene diamine system, the equilibrium was very far to the left (54). If the dielectric constants of the solvents involved are a measure of the "ionizing power" of the system, then the alcohols in the amines would show similar behavior.

This study points out that determinations (11) of temperature coefficients for the bimolecular rate constants for the proton transfer reactions may simply be a measure of the dependence of the "effective" alcohol concentration on temperature, since hydrogen bonds are known to be very temperature sensitive (55). Preliminary studies of dilute ethanol solutions in cyclohexane (done by the bulb technique), while interpretation is not straightforward, do indicate that the bimolecular rate constant for the protonation of $\phi_2^-$ by ethanol is at least 40 times greater than the value as determined in ethanol alone.

Admittedly, very few final conclusions can be drawn from this proton transfer study, but it is hoped that it points out the applicability of these reactions as a probe into the complexities of solvent structure effects.
APPENDIX

INTEGRATION OF RATE EQUATIONS FOR THE DECAY OF AN ABSORBER

The rate equation for a first-order or pseudo-first-order decay of an absorbing species \( a \) is given by:

\[
-d[a]/dt = k'[a]
\] (I)

where \( k' \) is the first-order constant. If \( [a]_0 \) is the concentration of \( a \) at zero time, which is defined as the end of the pulse, then, by integration:

\[
\int_{[a]_0}^{[a]} \frac{d[a]}{[a]} = -k' \int_0^t dt
\] (II)

\[
\ln([a]/[a]_0) = -k't
\] (III)

Substitution of \( [a] = D/e_a \) gives:

\[
-ln D = k't - \ln D_0
\] (IV)

where the D's are optical densities. A plot of \(-\ln D\) against time will be linear with slope \( k' \). The half-time, defined as the time required for the concentration of \( a \) to reach half its initial value, is given by:

\[
-ln(\frac{1}{2}[a]_0/[a]_0) = \ln 2 = k'\tau_{\frac{1}{2}}
\] (V)

from Equation III, or:

\[
\tau_{\frac{1}{2}} = 0.693/k'
\] (VI)

SECOND-ORDER DECAY

If \( a \) absorbs and decays by reaction with itself, or by reaction with \( b \) such that \([b]_0 = [a]_0 \) (and the stoichiometry is one to one for...
the latter reaction) then:

\[-d[a]/dt = k_s [a]^2\]  \hspace{1cm} (VII)

where \(k_s\) is the second-order constant for the reaction. Integration gives:

\[\int_{[a]_0}^{[a]} \frac{d[a]}{[a]^2} = -k_s \int_0^t dt\]  \hspace{1cm} (VIII)

\[\frac{1}{[a]_0} - \frac{1}{[a]} = -k_s t\]  \hspace{1cm} (IX)

Substitution of \(D/\epsilon_a d\) for \([a]\) gives:

\[\epsilon_a d/D = k_s t + \epsilon_a d/D_0\]  \hspace{1cm} (X)

\[1/D = (k_s/\epsilon_a d)t + 1/D_0\]  \hspace{1cm} (XI)

A plot of \(1/D\) versus time will be linear with slope \(k_s/\epsilon_a d\). From Equation IX the half-time is:

\[1/[a]_0 - 2/[a]_0 = -k_s \tau_{1/2}\]  \hspace{1cm} (XII)

\[\tau_{1/2} = \frac{1}{k_s [a]_0}\]  \hspace{1cm} (XIII)

EQUILIBRIUM REACTION

The rate equation for the decay of an absorbing species \(a\) involved in an equilibration with \(b\) is given by:

\[-d[a]/dt = k_f^a[a] - k_r^a[b]\]  \hspace{1cm} (XIV)

where \(k_f^a\) and \(k_r^a\) are the first-order or pseudo-first-order rate constants for the forward and reverse reactions, respectively. If \([a]_0 \gg [b]_0\) then:

\[[b] \approx [a]_0 - [a]\]  \hspace{1cm} (XV)

and at equilibrium

\[[a]_0 = [a]_{eq} + [b]_{eq}\]  \hspace{1cm} (XVI)

Substitution of XVI into XV and the resulting equation for \([b]\) into
Equation XIV gives:
\[-\frac{d[a]}{dt} = k_1[a] - k_2([a]_eq + [b]_eq - [a]) \tag{XVII}\]

But at equilibrium
\[-\frac{d[a]}{dt} = 0 = k_1[a]_eq - k_2[b]_eq \tag{XVIII}\]

and
\[[b]_eq = \frac{k_1[a]_eq}{k_2} \tag{XIX}\]

Substitution of XIX for $[b]_eq$ into Equation XVII gives:
\[-\frac{d[a]}{dt} = k_1[a] - k_1[a]_eq - k_1[a]_eq + k_2[a] \tag{XX}\]
\[-\frac{d[a]}{dt} = (k_1 + k_2)([a] - [a]_eq) \tag{XXI}\]

and integration yields:
\[
\int_{[a]_0}^{[a]} \frac{d[a]}{([a] - [a]_eq)} = -(k_1 + k_2) \int_0^t dt \tag{XXII}\]
\[
\ln \left( \frac{[a] - [a]_eq}{[a]_0 - [a]_eq} \right) = -(k_1 + k_2) t \tag{XXIII}\]

Substitution of $D/cd$ for $[a]$ and rearrangement gives:
\[-\ln (D - D_{eq}) = (k_1 + k_2) t - \ln (D_0 - D_{eq}) \tag{XXIV}\]

where $D_{eq}$ is the equilibrium optical density of $a$. A plot of
\[-\ln(D - D_{eq}) \text{ versus time is linear with slope } (k_1 + k_2).\]

**EQUILIBRIUM AND FIRST-ORDER REACTION**

Consider the rate equations for an absorber $a$ and a second species $b$ of the form:
\[-\frac{d[a]}{dt} = k_1[a] + k_2[a] - k_3[b] \tag{XXXV}\]
\[-\frac{d[b]}{dt} = k_4[b] + k_5[b] - k_6[a] \tag{XXXVI}\]

where the $k$'s are all first-order or pseudo-first-order rate constants.

Let $[a] = x$, $[b] = y$, $d[a]/dt = x'$, and so forth. Then XXV and XXVI become:
\[-x' = (k_i + k_f')x - k_i'y \quad \text{(XXVII)}\]
\[-y' = (k_{ii} + k_f')y - k_i'x \quad \text{(XXVIII)}\]

Solving Equation XXVII for \( y \) gives:

\[y = \frac{1}{k_i'} x' + \frac{(k_i + k_f')}{k_i'} x \quad \text{(XXIX)}\]

Differentiating with respect to time gives:

\[y' = \frac{1}{k_i'} x'' + \frac{(k_i + k_f')}{k_i'} x' \quad \text{(XXX)}\]

Substitution of XXIX and XXX into Equation XXVIII gives:

\[\frac{1}{k_i'} x'' + \frac{(k_i + k_{ii} + k_i' + k_f')}{{k_i'}} x' = \frac{k_i}{k_i'} - \frac{(k_{ii} + k_i')}{k_i'} x' \quad \frac{(k_i + k_i')(k_{ii} + k_i')}{k_i'} x \quad \text{(XXXI)}\]

Multiplication by \( k_i' \) and simplification yields:

\[x'' + (k_i + k_{ii} + k_i' + k_f')x' + (k_i'k_{ii} + k_i'k_i' + k_{ii}k_f')x = 0 \quad \text{(XXXII)}\]

The characteristic polynomial of this equation is:

\[p^2 + np + n = 0 \quad \text{(XXXIII)}\]

where \( m = (k_i + k_{ii} + k_i' + k_f') \) and \( n = (k_i'k_{ii} + k_i'k_i' + k_{ii}k_f') \). The roots of this equation are:

\[r_+ , r_- = \frac{-m \pm \sqrt{m^2 - 4n}}{2} \quad \text{(XXXIV)}\]

The solution of Equation XXXII then, if \( \alpha = -r_+ \) and \( \beta = -r_- \), is given by:

\[x = C_1e^{-\alpha t} + C_2e^{-\beta t} \quad \text{(XXXV)}\]

where the C's are functions of the k's and initial values of x and y.

Thus, the solution in terms of optical density of a is:

\[D = C_1'e^{-\alpha t} + C_2'e^{-\beta t} \quad \text{(XXXVI)}\]

Also,

\[(\alpha + \beta) = m = k_i + k_{ii} + k_f' + k_f' \quad \text{(XXXVII)}\]
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