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IN 1,2-DICHLOROBENZENE

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

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PLEASE NOTE:

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PUBLICATIONS

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Pulse radiolysis has been found to be a useful technique for the study of the optical absorption spectra and reaction kinetics of aromatic hydrocarbon radical ions in solution. When a $<10^{-1}$ M solution of an aromatic compound is irradiated, essentially all primary ionization processes involve solvent molecules (except in a case where the ionization potential of the solute is below the energy of the lowest excited state of the solvent (1)). However, it has been found that in a considerable number of solvents subsequent reactions lead to a significant and easily observable yield of aromatic radical ions.

The primary ionization process may be written

$$S_{\text{radiation}} \rightarrow S^+ + e^-$$

where $S$ is the solvent. (In some solvents there may be the formation of fragment cations as well.) Reaction 1 produces both positive and negative charge carriers which may lead to the formation of aromatic radical ions through reactions such as

$$S^+ + Ar \rightarrow S + Ar^+$$

$$e^-_{(\text{sol})} + Ar \rightarrow Ar^-$$

(where the electron is solvated in the case of a polar solvent). In cyclohexane, for example, both $Ar^+$ and $Ar^-$ are observed (2). However, if one of the charge carriers reacts readily with the solvent itself, to produce an ion that can no longer transfer an electron to
or from the aromatic molecule, only one of the aromatic ions will be formed.

In the alcohols the ionized solvent, ROH⁺, abstracts a hydrogen atom from the alcohol and forms ROH₂⁺, which does not ionize the aromatic solute. Thus only Ar⁻ is observed (3). Extensive studies (3-7) have been made of the reactions of many aromatic anions in a number of alcohol solvents.

There is evidence that a low energy electron can react with benzyl chloride dissolved in 3-methyl pentane (8), cyclohexane (9), or an alcohol (11) (in alcohol the electron is solvated) by a dissociative attachment reaction to produce chloride ions.

\[
e^{-}_{(\text{sol})} + \text{BzCl} \rightarrow \text{Bz}^+ + \text{Cl}^- \quad (4)
\]

It has been suggested (10-15) that after secondary electrons produced in Reaction 1 have been degraded in energy, they will react with a chlorinated alkane solvent, RCl, in a similar manner.

\[
e^- + \text{RCl} \rightarrow \text{R}^+ + \text{Cl}^- \quad (5)
\]

The Cl⁻ so produced will not transfer charge to an aromatic solute because of the higher electron affinity of the chlorine atom and the greater solvation energy of Cl⁻ compared with Ar⁻. Thus, at sufficiently high values of [RCl]/[Ar], this reaction will compete overwhelmingly with Reaction 3 and only the aromatic cation will be observed.

Aromatic hydrocarbon radical cations can be observed spectrophotometrically in the near-ultraviolet to near-infrared region of the spectrum. However the observation of particular optical absorption bands is not a sufficient criterion for identifying the absorber as
the aromatic cation, since in many cases the corresponding anion has a nearly identical absorption spectrum. This similarity of absorption spectra is expected on theoretical grounds (16), and has been observed experimentally (16-19) for anions and cations produced by chemical reduction and oxidation of the aromatic compound, respectively. Thus additional evidence is necessary for the identification of an aromatic cation in an irradiated solution where, in general, one must consider the possibility of the production of both cations and anions. The optical absorption spectrum will, however, provide a sufficient basis for distinguishing the aromatic radical cation from the triplet excited state (20), the hydrogen adduct radical (3), and protonated form (16) of the parent aromatic compound.

Arai, et al. (15) and Ueda (21) have observed the absorption spectra of a number of aromatic cations upon irradiation of $<10^{-1}$ M aromatic compound in a variety of chlorinated alkane solvents, in particular, in 1,2-dichloroethane (1,2-DCE). By studying the effects of various additives such as oxygen, nitrous oxide, ammonia, and aniline they were able to show that the absorption was, indeed, due to the aromatic cation and that no aromatic anion was formed. In addition, a large number of aromatic cation spectra have been observed (12, 13) in extensive studies of $\gamma$-irradiated polycrystalline carbon tetrachloride and glassy butyl chloride solutions at low temperatures, where the aromatic cations formed are stabilized in the matrix and can be observed by static methods.

In the investigation of Arai et al. (15) the major attention was given to the observation and identification of the aromatic cations.
produced in the radiolysis of 1,2-DCE and similar chlorinated alkane solutions. In addition a number of observations were made of various reactions involving the aromatic cation. It is the aim of this study to investigate these reactions more thoroughly with regard to their mechanisms and rates. Of particular interest is the determination, in this study, of the rate of charge transfer between a neutral aromatic molecule and an aromatic cation, since rate constants for this type of reaction are not known.

Previous investigators (11, 15, 21) of aromatic cations in chlorinated alkane solvents have suggested, in order to explain their findings, that the positive charge center may move through the solution not only by diffusion of the species \( RCl^+ \), but, more importantly, by a resonance charge transfer between the solvent and the solvent cation.

\[
RCl^+ + RCl \rightarrow RCl + RCl^+ 
\]  

Thus the positive charge may be able to move through the solution at a rate faster than the diffusion rate of the species \( RCl^+ \). Arai, et al. (15), using sub-microsecond time resolution, were able to measure a lower limit for the rate of formation of the aromatic cation. This study extends the observation to a tenfold shorter time scale in seeking evidence for Reaction 6, and considers other possible reactions of the positive charge carrier besides Reaction 2.

Arai, et al. (15) and Ueda (21) have made somewhat different observations of the mode of disappearance of the aromatic cations, which decay on a microsecond time scale, and have suggested different forms for the counter ion (the product of Reaction 5). This study investigates further the mechanism and rate of the disappearance of the
aromatic cation produced in irradiated 1,2-DCE solution.

Finally, Arai, et al. (15) observed the occurrence of reactions of the type
\[ \text{Ar}_a^+ + \text{Ar}_b^- \rightarrow \text{Ar}_a^- + \text{Ar}_b^+ \] (7)
where \( \text{Ar}_a \) and \( \text{Ar}_b \) are two different aromatic compounds. In this study the rate constant for Reaction 7 is measured for several aromatic pairs.

It will be of interest to compare these rates with those for reactions of the type
\[ \text{Ar}_a^- + \text{Ar}_b^+ \rightarrow \text{Ar}_a^+ + \text{Ar}_b^- \] (8)
Reactions of this type have been studied extensively in isopropyl alcohol (5,7) and their rate constants found to correlate well with relative values calculated from a theory of electron transfer put forth by Marcus (22-29). This theory is equally applicable for calculating relative rate constants for Reaction 7.

All experiments in this study were done using 1,2-DCE as solvent. The work of Arai, et al. (15) and Ueda (21) has shown that very similar results are to be expected in certain other chlorinated alkane solvents such as 1,1-dichloroethane; 1,1,2-trichloroethane; 1,1,2,2-tetrachloroethane; and n-butyl chloride. On the other hand, they found very different behavior in the solvents carbon tetrachloride; 1,1,1-trichloroethane; pentachloroethane; and to a lesser extent in chloroform. In these latter solvents the absorption spectrum was not that of the aromatic cation, so that some other species must be formed. Other studies (30-33) in irradiated, liquid carbon tetrachloride
solutions have found absorptions due to species other than the aromatic cation. It is interesting to note, as Ueda (21) has pointed out, that the solvents found to behave differently from 1,2-DCE all have a \(-\text{CCl}_3\) group. Also Duhler and Ebert (31), who observed optical absorption bands in carbon tetrachloride solutions which they attributed to charge transfer complexes, found that the yield of these species decreased with the decreasing number of chlorine atoms in a series of chlorinated methanes.

By contrast, at 77°K, irradiation of polycrystalline carbon tetrachloride containing aromatic solutes (11,12) gives the aromatic cation. However, in the rigid media the positive charge carrier may be quite mobile, by Reaction 6, while other products of carbon tetrachloride irradiation may be trapped by the matrix and unable to react with the aromatic solute. Thus the results observed in rigid media may differ significantly from those observed in fluid solution.

It appears, therefore, that the results of this study can be generalized to some, but not all, chlorinated alkane, liquid solvents.
EXPERIMENTAL PROCEDURES

The general techniques of pulse radiolysis used in this study have been described previously (31,35). The following description will give details of the particular equipment and methods used in this investigation.

PULSE IRRADIATION

A Varian V-7715A electron linear accelerator was used as a source of high energy electrons. The electron energies can be varied in the range 2 to 6 keV. Two types of pulses were used: a 325 mA current pulse with electron energies from 3 to 4 keV, and a 600 mA current pulse with 1 to 1.5 keV electrons. The latter pulse was used only for the investigation of the formation of the aromatic cations.

Figure 1 shows the time profile of two typical pulses. The rise and decay times of the pulse are approximately 6 nanoseconds, so that the end of the energy injection into the cell is clearly defined. The length of the 325 mA pulse is continuously variable from 1.4 nsec to 50 nsec, and that of the 600 mA pulse from 1/0 nsec to 30 nsec. The rise and decay times are independent of pulse length. During a day's experiment the pulse current remained constant within ±7%, so that the dose was proportional to the pulse length.

The rectangular irradiation cell was made of fused quartz and had optical end windows made of high purity silica, which is very
Figure 1: Time profile of 325 mA electron pulses. The current was measured as a function of time with a Faraday cup placed in the position normally occupied by the cell.
resistant to the formation of color centers when irradiated. The thickness of quartz on the side exposed to the electron beam was about 1 mm. The internal dimensions of the cell were 8 mm in the direction of the electron beam, 12 mm in the vertical direction, and 20 mm in the direction of the light beam. Thus the depth of the cell is shorter than the range of the 3-4 kev electrons.

The cell was connected, through a 6 mm inner diameter tube with graded seal, to a 100 ml Pyrex storage bulb, as shown in Figure 2. Solutions were introduced into the bulb through a stopcock with a teflon plug. During an experiment the cell assembly was supported with the cell at the bottom. Between electron pulses the cell was tipped and its contents thoroughly mixed with those of the bulb to dilute any stable products of the radiolysis. A volume of solution was placed in the bulb approximately equal to the product of the cell volume and the number of pulses used. There was no trend, due to product build-up or reactant depletion, in the rate of reaction from pulse to pulse when this technique was used. Even when the cell was pulsed many times without tipping, there was little, if any, change in the decay kinetics of the aromatic cation.

For the 325 ma pulse it has been shown (36) that, due to scattering of the electron beam by the quartz wall of the cell, the radiation received by the solution is approximately uniform—as judged by the darkening of polyvinyl chloride—over its entire area in the plane perpendicular to the electron beam. Furthermore, the dose absorbed by ethanol is approximately constant through the depth of the cell, i.e., in the direction of the electron beam. The dose absorbed by
Figure 2: Irradiation cell with attached solution storage bulb.
the last 2 mm of ethanol is about 90% of the dose absorbed by the first 2 mm, with the absorption in the center of the cell being nearly equal to that of the front of the cell.

Sauer (37) and Boag (38) have discussed the influence of a non-uniform distribution of reactants on the measurement of a rate constant by the methods of this study. The measurement of a first-order or pseudo-first-order rate constant is affected only by non-uniformity across the light beam and, for the above distribution, will be in error by less than one per cent. The measurement of a second-order rate constant is affected by non-uniformity both along and across the light beam. The combined error with the above distribution will be, at most, a few per cent; this is small compared to other errors in the determination of the one second-order rate constant measured in this study.

The absorbed dose in water has been found (39) to be $6 \times 10^{16}$ ev/g for a 0.1 μsec, 325 ma pulse. However, a knowledge of the absorbed dose, in the present case in 1,2-DCE, is not needed for the interpretation of the results obtained in this study.

In most experiments the temperature of the cell was the ambient temperature of the radiation room, which was kept constant within ± 1 degree centigrade by an air conditioning unit. The apparatus and technique for the low temperature experiment have been described by Arai, et al. (6). The cell was mounted in an insulated brass box which had a thin copper window to admit the electron beam. Two evacuated cylindrical quartz cells placed in opposite walls served as windows for the analyzing light beam, which passed once through the
cell. A stream of dry nitrogen gas was passed through a copper coil immersed in liquid nitrogen and then into the insulated box below the cell. The temperature of the cell was measured with a copper constantan thermocouple cemented with epoxy resin to the outside of the top of the cell. The temperature could be varied by adjusting the flow rate of the nitrogen gas.

OPTICAL DETECTION

The concentration of transient species produced by the radiation was followed by spectrophotometric measurement of the optical density of the solution. Figure 3 is a schematic diagram of the optical system. The light source was a Type XBO/50W Osram 500 watt xenon lamp. The output of the lamp was constant within ±1% during the time of any measurement and in general was stable for many minutes. A remote controlled shutter prevented the light from striking the cell except for a few seconds at the time of a pulse. This, together with appropriate short-wavelength Corning filters placed between lamp and cell, kept any possible photodecomposition of the solution at a minimum. At the time of a pulse the light was passed twice through the cell in a direction perpendicular to that of the electron beam. After passing through an appropriate Corning filter, to remove all wavelengths less than or equal to one half the desired wavelength, it was focused on the entrance slit of a Bausch and Lamb grating monochromator. The following gratings were used, depending on the wavelength region of interest: Type 33-36-01, wavelength region 180-400nm, 2700 grooves/mm, dispersion 3.2 nm/mm of exit slit
Figure 3: Schematic diagram of the optical arrangement.
width; Type 33-86-02, 350-300 nm, 1350 grooves/mm, dispersion 6.4
nm/μm; Type 33-97-07, 200-700 nm, 1200 grooves/mm, dispersion 7.4
nm/μm; and Type 33-96-03, 700-1600 nm, 675 grooves/mm, dispersion 12.8
nm/μm. The calibration of the gratings was checked against the emission of a medium pressure mercury lamp.

When desired, two wavelengths could be monitored simultaneously by splitting the light beam with a partially reflecting chromium on quartz mirror and focusing it onto two monochromators. This was done only for spectral rapping, when the second monochromator was kept at a fixed wavelength and its output used to measure electron pulse reproducibility.

The light from the monochromator exit slit struck the photocathode of a photomultiplier tube which was shielded by one-half inch of lead to reduce radiation interference. RCA 7102, 7200, and 1P28 photomultiplier tubes, with S-1, S-19, and S-5 spectral responses respectively, were used. The output of the photomultiplier tube was coupled to the oscilloscope through a Nexus Model FSL12 signal conditioning amplifier which allows direct coupled steady state operation into a 93 ohm transmission line. A shielded cable transmitted the signal to the oscilloscope, which was outside the radiation area.

Both the power to the Nexus amplifier and the high voltage supply to the photomultiplier were filtered electronically to prevent radio frequency interference, generated by the linear accelerator, from entering the detection system and causing noise on the signal.

The linearity of the Nexus amplifier output with light intensity input was checked in the following way. A low intensity light pulse
from a gallium arsenide lamp was beamed onto the photocathode along with a higher intensity, continuous light, and the amplifier output observed on an oscilloscope. The height of the output pulse remained constant as the intensity of the continuous light was varied from zero up to a level that produced greater than 1.5 volts output into a 93 ohm load. For most experiments the light intensity was adjusted so that the amplifier output was less than 0.6 volts into a 93 ohm load, i.e., well within the linear response range of the system.

The electronic signal was displayed on the screen of a Tektronix Type 555 dual beam oscilloscope. This allowed the signal from one photomultiplier to be observed on two different time scales and/or at two different vertical amplifications. Alternatively, if two photomultipliers were used, one could observe the signal from two different light wavelengths simultaneously. The oscilloscope traces were photographed with a Tektronix C-12 Polaroid five-inch oscilloscope camera using Type 107 Polaroid 3,000 or 10,000 speed film.

The horizontal sweep of the oscilloscope over the middle eight centimeters of the screen was linear with time to within 2½%. The time base of the oscilloscope was calibrated using a Tektronix Type 184 time mark generator, which takes its time base from a crystal kept at constant temperature. This calibration was done frequently and showed the oscilloscope time base to be stable over a period of several months. The vertical scale of the oscilloscope was calibrated using an internal calibrating voltage. Since all measurements were difference measurements, as explained under "Data Analysis," the
absolute calibration of the vertical scale was not necessary. It was sufficient to know the ratio of the vertical sensitivities of the two channels.

Since many measurements were made on sub-microsecond time scales, careful attention was given to the time response characteristics of the detection system. The rise time of the total system described above was found to be about 100 nsec. This is the time required for the output to rise from 10% to 90% of full deflection when the input is an "instantaneous" step function. The signals observed in this study were not step functions, however, but more slowly changing exponentially or similarly decaying signals. Thus the system will follow within better than one per cent an exponential decay whose half-life is greater than 200 nsec. In most experiments, concentrations could be adjusted so that the kinetics were slower than this.

For measurements that required faster detection, namely those of the rate of formation of the aromatic cations, a modified detection system was used similar to that of Hunt and Thomas (4:0). Since the signal conditioning amplifier is the slowest part of the usual detection system, it was removed and the photomultiplier coupled directly to the oscilloscope. This faster system utilized the photomultiplier in a high anode current, short duty cycle mode of operation. The response time of such a system is limited only by the photomultiplier anode response and the oscilloscope response. To achieve a short duty cycle and prevent anode overload, a light chopper was placed between Lens 2 and the monochromator. The chopper was made from an opaque 9 cm radius disc which was rotated in a plane perpendicular to
that of the light beam. A one centimeter notch in the edge of the
disc allowed the light to pass for 0.5 usec out of every 16.7 usec.
The chopper disc was rotated continuously and the accelerator synchro-
nized to pulse while the chopper was transmitting light.

The linearity of the photomultiplier output with light inten-
sity input in this system was checked in the following way. If a
solution of benzyl chloride in ethanol is irradiated with a short
pulse, one observes, at 317 nm, very little emission or absorption
during the pulse except a strong emission of Čerenkov light. If
the photomultiplier is responding linearly, the output due to this
Čerenkov pulse should be the same whether the background light level
is zero or some positive value, i.e., whether the lamp shutter is
closed or open. Figure 4 shows the photomultiplier output voltage
into a 50 ohm load produced by the Čerenkov pulse when the lamp shut-
ter was open divided by that when the lamp shutter was closed plot-
ted versus the total output voltage, i.e., from lamp light plus
Čerenkov pulse. The device shows good linearity if the output volt-
age is below 0.5 volts. During an experiment the output voltage was
kept below this value by an appropriate setting of the monochromator
exit slit width.

The Tektronix oscilloscope was also too slow for the fast meas-
urements, so a Fairchild Type 777 dual beam oscilloscope was used
instead. The rise time of this faster detection system was less than
10 nsec.
Figure 4: Test for the linear response range of the fast 1P28 detector. $V_o$, output voltage (into a 50 ohm load) produced by the lamp light; $V_C$, output voltage produced by the Čerenkov light pulse when the lamp shutter is closed; $V_{CI}$, output voltage produced by the Čerenkov light pulse when the lamp shutter is open.
MATERIALS AND SOLUTION PREPARATION

The 1,2-dichloroethane was Matheson, Coleman, and Bell reagent grade. For most experiments it was purified in the following way. A 400-500 ml volume was washed with 100 ml of concentrated sulfuric acid ("Baker Analyzed" reagent grade) to remove alcohol stabilizer. Next it was washed with doubly distilled water and then with approximately 1 l of sodium hydroxide. (The NaOH solution was prepared from a 19.4 M solution and freshly boiled, triply distilled water and then stored in a tight container so as to be relatively free from CO₂.) Following four or five washes with doubly distilled water, the 1,2-dichloroethane was dried over powdered barium oxide (Baker and Adamson technical grade). Finally it was passed through a freshly prepared 2.1 X 40 cm column of Dowel neutral aluminum oxide and used within two days with a minimum exposure to light and air.

For experiments designed to measure the rate of aromatic cation formation, several other purifying techniques were used in conjunction with, or instead of, the above procedure. In one such experiment, in order to remove any carbonyl impurities, the 1,2-dichloroethane obtained by the above process was saturated with 2,4-dinitrophenylhydrazine and passed twice through a 2,4-dinitrophenylhydrazine, H₃PO₄, Colite column prepared in the manner of Schwartz and Parks (1). The eluant was distilled through a two meter column packed with glass wool and the middle fraction (about 60%) collected. This was placed in a 3.2 X 25 cm bottle and lowered slowly over a period of hours into liquid nitrogen. When most of the liquid was frozen, the remaining liquid at the top was discarded and the solid
was then allowed to melt. This was repeated three times. All purification methods, however, gave roughly the same results in terms of the yield of aromatic cation as a function of neutral aromatic molecule concentration. As will be discussed later, this functional relationship is a measure of solvent cation lifetime and hence an indication of possible impurities that can neutralize this ion.

Biphenyl, para-terphenyl, naphthalene, and anthracene were zone refined materials supplied by James Hinton. On the basis of several analysis methods, including vapor-phase chromatography, he rates them as being 99.99% pure. Pyrene supplied by Hinton was rated as 99.8% pure. Those compounds were all used without further treatment or purification.

Tetrastilbene ammonium chloride was from Eastman Organic Chemicals. After recrystallization from 1,2-DCE, it was dried under vacuum at 90°C and handled in a dry nitrogen atmosphere because it is very hygroscopic.

For most experiments solutions of a desired concentration were prepared by weighing an appropriate amount of a single solute into a 50 ml volumetric flask and adding solvent. The top of the flask was fitted with a 14/35 outer standard taper. A pipet was fitted with an inner taper as shown in Figure 5 and could thus serve as a stopper for the flask as well as to draw off the solution. Stopcocks at the top of the pipets made it possible to seal off the system except during pipetting. This prevented evaporation losses or possible moisture pickup during the course of a day's experiment. Three such flasks with fitting pipets were constructed: one with a 5 ml pipet,
Figure 5: Volumetric flask with fitted pipet used to prepare two-solute solutions.
one with a 0-4 ml graduated pipet, and one with a 0-9 ml graduated pipet.

For many experiments it was desired to make a series of solutions in which one solute, $a$, was kept at constant concentration, while the second solute, $b$, had its concentration varied over a 10- to 40-fold range. This was accomplished in the following way. A solution of $a$ was placed in the flask with a 5 ml pipet, a solution of $b$ was placed in the flask with a 0-4 ml pipet, and pure solvent was placed in the remaining flask. Five milliliters of a solution and from 0.1 to 4 ml of $b$ solution were pipetted directly into the storage bulb of the cell. Then an amount of solvent was added to bring the total volume of solution to 11 ml. Thus $[a]$ was constant and $[b]$ was proportional to the volume of $b$ solution added. When an experiment with one such two-solute solution was finished, the cell bulb was emptied and the next solution made into it. (When calculating $[b]$, a correction was made for the small residual amount of the previous solution remaining in the cell bulb.)

For experiments involving only one solute, where a greater concentration range was desired, a different technique was used. A solution of the highest desired concentration was prepared in a volumetric flask. A small fraction, e.g., one-tenth, of this was pipetted into a second volumetric flask of equal size, and the experiment performed with the remaining solution. The second volumetric flask was then filled and the same fraction of its contents pipetted to a third flask. By continuing this procedure one could prepare solutions of concentrations, e.g., $10^{-2}$ M, $10^{-3}$ M, $10^{-4}$ M, etc.
Most solutions were not degassed in any way. An experiment performed with three solutions of $10^{-2}$ M biphenyl in 1,2-dichloroethane—one which had been flushed by bubbling with argon, one in equilibrium with air, and one flushed with oxygen—showed that the oxygen content of the solution had little effect on the yield or decay of biphenyl cation. The decay rate became only very slightly slower as the oxygen concentration was increased. This was also the observation of Arai, et al. (15).

DATA ANALYSIS

Pictures from the oscilloscope camera were sometimes analyzed directly, but were usually enlarged two times in linear dimensions as photostatic prints for more accurate analysis. The quality of the enlargement was checked by looking for distortion in the grid lines on the picture. Data points were measured by attaching a transparent millimeter grid to the picture, or with a vernier caliper.

Figure 6 shows two representative oscilloscope pictures. One channel of the oscilloscope writes three traces in connection with each electron pulse. The lower trace is made with the lamp shutter closed and represents 0% transmission of light. The upper, horizontal trace is made with the lamp shutter open, but with no electron pulse, and represents the transmission, $I_0$, of the non-irradiated cell. The electron pulse is triggered just after the beginning of the third trace, which is written with the lamp shutter open and shows any change in transmitted light intensity, $I_t$, produced by the irradiation. The third trace is automatically triggered 5 msec after the
Figure 6: Typical oscilloscope pictures; (a) Decay of an absorber formed during the pulse, (b) Formation and subsequent decay of an absorber.
upper trace so as to minimize the possibility of a lamp fluctuation between the two traces. By scanning the trace during a pulse, but with the lamp shutter closed, one can observe and light emitted by the solution during or after the electron pulse.

When the absorption produced by the irradiation is small, the signal displayed by the bottom channel of the oscilloscope can be multiplied electronically by a factor of two or four. This, however, places the bottom trace off scale. But if the vertical scale of the top channel is one-half or one-fourth of that of the bottom channel, one can use the top channel's display to measure $I_o$ and the bottom channel's display to measure the changes produced by the irradiation. The error in $I_o$ measured in this way is less than ±5%.

From the oscilloscope picture one can measure the transmitted light intensity, $I_t^\lambda$, at the wavelength, $\lambda$, set by the monochromator, as a function of time, $t$. One would like to calculate two quantities from this: one is the concentration, $[a]_t$, of the absorbing species, $a$, as a function of time and the other is the ability of $a$ to absorb light as a function of $\lambda$.

If the Beer-Lambert Law is obeyed by a single absorbing species, $a$, then for monochromatic light of wavelength $\lambda$

$$D_t^\lambda = \log_{10}(I_o^\lambda/I_t^\lambda) = \epsilon_a[a]_t$$

where $D_t^\lambda$ = the optical density and is defined by the first equality,

$I_o^\lambda$ = transmitted light intensity at wavelength $\lambda$ when no $a$ is present,

$I_t^\lambda$ = transmitted light intensity at wavelength $\lambda$ when $a$ is present, which will vary with time if $[a]$ does,
\[ \varepsilon^\lambda_a = \text{a proportionality constant with units of N}^{-1} \text{ cm}^{-1}, \text{ called the molar decadic extinction coefficient, which depends on the species a,} \]

\[ [a]_t = \text{the concentration of a, which may vary with time,} \]

\[ d = \text{the length of the light path through the solution.} \]

The middle quantity is calculable from the oscilloscope pictures and, for the optical arrangement of Figure 3, \( d = 2(\text{cell length})(\sec \phi/2) \]

\[ = 2.00 \times 2(\text{cell length}) = 4.0 \text{ cm}. \]

Thus one obtains the product, \( \varepsilon^\lambda_a [a]_t \), of the two desired quantities. In a given picture, where \( \lambda \) is constant, this product is proportional to \( [a]_t \). On the other hand, at constant dose and a fixed time after the pulse, \( [a]_t \) is constant and the product is proportional to \( \varepsilon^\lambda_a \). Since in general one does not know the amount of species a produced by the pulse, the data does not give either factor absolutely. However, for much of this study it was sufficient to know only relative changes of \( [a]_t \) with time or of \( \varepsilon^\lambda_a \) with \( \lambda \). In the experiments where \( [a]_t \) was needed absolutely, \( \varepsilon^\lambda_a \) was obtained from other work.

If there is more than one absorbing species in the solution, Equation I becomes

\[ d^\lambda = \log_{10}(I^\lambda_o/I^\lambda_t) = \{\varepsilon^\lambda_a [a]_t + \varepsilon^\lambda_b [b]_t + \ldots\}d \quad (II) \]

and the data yields only the quantity \( \{\varepsilon^\lambda_a [a]_t + \varepsilon^\lambda_b [b]_t + \ldots\} \).

The validity of the application of the Beer-Lambert Law in the present study must be examined carefully. If the irradiation of the cell produces any emission of light of wavelength \( \lambda \) or a bleaching of any absorber in the solution or cell windows, this will lead to an inaccurate measurement of \( I^\lambda_t \) or effective \( I^\lambda_o \) respectively. One can
check for emission by irradiating the cell with the lamp shutter closed. He can check for bleaching by observing if the Cerenkov light intensity is greater when the lamp shutter is open or by noting whether the trace after the pulse decays to a point above the $I_0^\lambda$ trace.

When light in the visible region of the spectrum was monitored with the usual photomultiplier, Nexus amplifier setup, a small emission—probably due mostly to Cerenkov light—was observed during the pulse, and this emission was more intense when the lamp shutter was open. However, this apparent bleaching may have been an artifact of the system since it depended very little on the contents of the cell or the wavelength of light. In any case, the emission and apparent bleaching occurred only during the pulse and all measurements with this system were made after the end of the pulse. Furthermore, no traces after the pulse were observed to decay to a point above the $I_0^\lambda$ trace. When the faster detection system was used to observe events during and immediately after the pulse, no apparent bleaching was observed. The signal observed with the lamp shutter closed was subtracted from the signal with the lamp shutter open to give the true transmitted light intensity, $I_0^\lambda$.

If any light, $J$, which has not passed through the solution strikes the photomultiplier, one will measure $(I_0^\lambda + J)$ and $(I_0^\lambda + J)$ and the ratio of these quantities will be different from $I_0^\lambda/I_0^\lambda$. Thus for Equation I to be valid, $J$ must be kept as small as possible. To accomplish this, all lights in the radiation room, except the xenon lamp, were turned off. There is still the problem of stray light and
of light reflected from the front optical window of the cell. One can measure the amount of this reflected light by removing Mirror 1 in Figure 3. It was found to be not more than two per cent of $I_0$ over the wavelength region of this study.

Since $\lambda$ in this study was in the visible and near-infrared regions of the spectrum, scattered light, i.e., light of a wavelength other than the band at $\lambda$ which passes the monochromator due to the imperfection of the device, was assumed to be negligible. Furthermore, an appropriate Corning filter prevented light of wavelengths $\lambda/2, \lambda/3, \lambda/4$, etc. from entering the monochromator.

The derivation of Equation I assumes that the molecules of absorber do not associate with each other. In this study the absorbing species are aromatic cations at a concentration of less than $10^{-5}$ M. This low concentration, as well as the like charge on the ions, makes any association unlikely.

As will be discussed later, there is some evidence for the association of certain aromatic cations with their parent neutral molecules. This association, however, forms a new species so that Equation II is now applicable.

Equation I is derived assuming a uniform distribution of the absorber throughout the bulk of the cell. As shown above, this is approximately true; and the effects on Equation I and hence on the measurement of a rate constant of a non-uniform distribution have been considered.

Finally, the derivation of Equation I assumes that the light is strictly monochromatic. However, the monochromator allows light to
pass over a certain bandwidth, $\lambda_1$ to $\lambda_2$. Let $d\lambda$ be the transmitted light intensity in the wavelength region $\lambda$ to $\lambda + d\lambda$. For infinitesimal $d\lambda$, the light may be considered monochromatic in this region so that Equation I (or II) is valid. Written in a rearranged form it becomes

$$dI_t^\lambda = \exp(-\epsilon_\lambda[a]_t d) dI_0^\lambda$$  \text{(III)}

Integration over the monochromator bandwidth gives

$$\int_{\lambda_1}^{\lambda_2} dI_t^\lambda = I_t = \int_{\lambda_1}^{\lambda_2} \exp(-\epsilon_\lambda[a]_t d) dI_0^\lambda$$  \text{(IV)}

where $I_t$ is the measured transmitted light intensity. Suppose that $\epsilon_\lambda$ is approximately constant over the region $\lambda_1$ to $\lambda_2$. Then Equation IV becomes

$$I_t = \exp(-\epsilon_\lambda[a]_t d) \int_{\lambda_1}^{\lambda_2} dI_0^\lambda$$  \text{(V)}

$$I_t = \exp(-\epsilon_\lambda[a]_t d) I_0$$  \text{(VI)}

Rearrangement gives

$$D_t = \log_{10}(I_0/I_t) = \epsilon_\lambda[a]_t d$$  \text{(VII)}

This equation has the same form as Equation I, but is now in terms of the measured quantities $I_0$ and $I_t$.

It remains to examine the approximation that $\epsilon_\lambda$ is constant over the range $\lambda_1$ to $\lambda_2$. The separation of $\lambda_1$ and $\lambda_2$ is determined by the width of the exit slit of the monochromator and the dispersion of the grating. In this study the exit slit was kept as narrow as the desired $I_0$ value would permit, but was never wider than to give a maximum total dispersion of 22 nm. For most kir studies the total dispersion was less than 10 nm. The spectra ($\omega$, of the species
observed in this study exhibit, in general, broad absorption bands; so that, in the neighborhood of a band peak, the value of $\varepsilon_\lambda$ is nearly constant over the monochromator bandwidths used. Thus Equation VII is sufficiently accurate and may be used to calculate $\varepsilon_\lambda(a)$ from the oscilloscope pictures.
RESULTS AND DISCUSSION

OBSERVATION OF AROMATIC CATIONS

As discussed in the Introduction, 1,2-dichloroethane (1,2-DCE) solutions of four aromatic hydrocarbons have been pulse irradiated (15,21) and measurements made of the resulting absorption spectra in the near-ultraviolet to near-infrared region of the spectrum.

With biphenyl as solute (5 x 10^{-2} - 10^{-3} M) two absorption bands were observed after a 0.5 μsec pulse—one at 320 nm and a weaker one at 620 nm. Above 400 nm the decay characteristics of the absorption were independent of wavelength which indicated that only one species was absorbing the light. Below 400 nm there was a small contribution to the absorption from a longer-lived species. A similar spectrum was observed with 1,1,2-trichloroethane as solvent. This spectrum is characteristic of the biphenyl radical ion (15) and the effects of the additives O_2, H_2O, NH_3, and aniline show that only the biphenyl cation is present. (Certain additives, such as O_2 and H_2O, reduce the yield and/or the lifetime of aromatic anions produced by the radiolysis of alcohol solutions. Other additives, such as aniline, do not react with the aromatic anions. In 1,2-DCE and 1,1,2-trichloroethane these additives have exactly the opposite effect on the biphenyl ion produced. Thus the ion must be the biphenyl cation.)

With 4.3 x 10^{-2} μ-terphenyl as solute, an absorption band was observed at 425 nm, with a shoulder at 455 nm; a second band was
observed at 965 nm. Both bands show identical decay characteristics and are therefore due to a single absorbing species. This spectrum is characteristic of the p-terphenyl radical ion and the effects of O₂, aniline, and diphenylamine additives show that the absorber is the p-terphenyl cation.

With 5 X 10⁻³ M anthracene solute an absorption band was observed at 725 nm. Anthracene cation, produced by chemical oxidation, has an absorption band at this wavelength (1,2). The effect of O₂ additive in the irradiated solution shows that the absorption is due to the cation rather than the anion.

The observed aromatic cation spectra are very similar in general shape to those of the respective anions, which are observed in irradiated alcohol (3) and tetrahydrofuran (1,3). However there are detectable differences in the position of some band peaks, especially between the near-infrared band peak of the p-terphenyl cation (965 nm) and the p-terphenyl anion (870 nm).

Thus in irradiated 1,2-DCE solutions, observation of the 690 nm band, the 965 (or 955) nm band, and 725 nm band will allow one to follow the concentration changes of the biphenyl, p-terphenyl, and anthracene cations respectively. This was the method used for studying the reactions of these cations in the present work. Few observations were made of the shorter wavelength bands of the biphenyl and p-terphenyl cations because of other species absorbing below 400 nm and 320 nm in the biphenyl and p-terphenyl solutions respectively. In addition this selection of longer wavelengths precluded the
possibility of interference from the absorption of any triplet excited aromatic molecules (20).

FORMATION OF THE AROMATIC CATION IN 1,2-DCE

In all experiments the rate of formation of the aromatic cation was too fast to be observed, i.e., there was no detectable growth in optical density after the end of the electron pulse. On the other hand, the lifetime of the aromatic cation was much longer than the length of the pulse. Thus the optical density, $D_p$, measured at the end of the pulse was proportional to the yield of aromatic cation for the given dose. Figure 7 is a plot of $\log D_p$ versus $\log [Ar]$ for biphenyl and p-tolophenyl solutions. These results are very similar to those of Arai, et al. (15) (Figure 7) and Ueda (21) for the trans-stilbene cation in 1,1-dichloroethane and in n-butylchloride. For $[Ar] > 2 \times 10^{-2}$ M practically all of the precursor, P, of the aromatic cation is scavenged by the aromatic compound.

$$P + Ar \rightarrow P^- + Ar^+ \quad (9)$$

Previous investigators (11,15,21) have suggested that P is the solvent cation, in this case 1,2-DCE⁺, produced by the primary ionization step. The possibility that P is a chlorine atom, produced by dissociation of an excited solvent molecule, seems to be ruled out for two reasons. First, evidence will be presented later that chloride ion reacts very rapidly with Ar⁺. Thus if P = Cl⁺, the products of Reaction 9 would react with each other as soon as they were formed and very little Ar⁺ should be observed. In addition, Buhler, et al. (31) have reported the optical absorption spectra of charge transfer
Figure 4. The effect of concentration of 1-stilbene on the yield of the stilbene cation in 1,1-DCE and n-butylchloride. The optical density at 490 nm is shown as a function of concentration. This optical density was observed in the microsecond region and extrapolated back in time to the end of the pulse.

Figure 7: Relative radiolysis yield of Ar$^+$ as a function of Ar concentration in 1,2-DCE solution. The graph is a plot of log PA versus log[Ar]. O, Ar = biphenyl, $\lambda$ = 655 nm, p = 90 nsec, T = +25°C; □, Ar = p-torphenyl, $\lambda$ = 452 nm, p = 140 nsec, T = -31°C (T = +23°C for 1 to achieve solution). The p-torphenyl points are displaced upward by log 2 for clarity of presentation. The solid curves are calculated as described in the text. The insert is taken from Reference 15 with permission of the authors.
complexes observed following the irradiation of liquid CCl₄ solutions of a number of aromatic compounds. They suggest that chlorine atoms, produced by the radiolysis, react with the aromatic molecules to produce those complexes. The spectra they observe are clearly different from those of the cation spectra observed in 1,2-DCE and similar solvents.

Taking P to be the solvent cation, Reaction 9 becomes

\[ 1,2\text{-DCE}^+ + \text{Ar} \rightarrow 1,2\text{-DCE} + \text{Ar}^+ \] (10)

and one would like to know the value of the rate constant, \( k_{10} \), for this reaction, defined by

\[ \frac{d[\text{Ar}^+]}{dt} = k_{10}[\text{Ar}][S^+] \] (VIII)

where \( S^+ = 1,2\text{-DCE}^+ \). As will be shown later, the value of this rate constant gives some information concerning the detailed mechanism of Reaction 10. Since this equation involves \( [S^+] \), one must consider whether any other reactions cause \( [S^+] \) to change while Reaction 10 is occurring, i.e., whether there are other decay modes of \( S^+ \). Some possible reactions include

\[ S^+ + \text{counter ion} \rightarrow \text{neutralization} \] (11)

and

\[ S^+ + I \rightarrow S + I^+ \] (12)

where \( I \) is an impurity whose cation does not readily transfer charge to the aromatic solute. Since \( S^+ \) may possibly decay by a number of such reactions, the natures of which are only speculative, an exact calculation of \( [S^+] \) as a function of time is not possible.

However, several approximate methods for estimating \( k_{10} \) are available. One is to assume, as a first approximation, that
Reaction 10 is much faster—at the value of [Ar] used—than any of the other reactions of S⁺. Arai, et al. (15), using a method which effectively made this approximation, found that $k_{10} > 10^{10} \text{ M}^{-1} \text{sec}^{-1}$ for (1,1-dichloroethane)⁺ plus t-stilbene with [t-stilbene] equal to $3 \times 10^{-4} \text{ M}$. They were able to obtain only a lower limit for $k_{10}$ since the reaction was too fast to follow the growth of [Ar⁺]. However, as seen in Figure 7, at this value of [t-stilbene] the yield of t-stilbene cation was only 0.4 of the yield at higher [t-stilbene]. This suggests that with [t-stilbene] equal to $3 \times 10^{-4} \text{ M}$ there are other reactions competing significantly with Reaction 10 to produce decay of S⁺. On the other hand, with [t-stilbene] equal to $10^{-2} \text{ M}$ the competing reactions were negligible (the yield curve had reached the saturation point), but the lower limit determined for $k_{10}$ was only $3 \times 10^5 \text{ M}^{-1} \text{sec}^{-1}$. Thus a more accurate approximation must consider Reactions such as 11 and 12.

A more accurate approximation is to assume that the decay of S⁺, when Ar is absent (i.e., by Reactions 11, 12, etc.), is pseudo-first-order. If Reactions such as 12 predominate, this will be a highly accurate approximation. As little as 0.01% of an impurity in the solvent, which reacts rapidly by Reaction 12 but does not readily transfer charge to the aromatic solute, could lead to the observed results. This impurity level is quite possible in the solvent used here. On the other hand, if Reactions such as 11 predominate, the approximation will be less accurate since Reaction 11 is equivalent to a second-order decay of S⁺.
Using this approximation we may write the following reaction scheme:

\[
\begin{align*}
S & \xrightarrow{\text{radiation}} S^+ + e^- \\
S^+ + Ar & \rightarrow S + Ar^+ \\
S^+ & \rightarrow \text{products}
\end{align*}
\]

where Reaction 114 represents all the decay modes of \( S^+ \) (except Reaction 10), the sum of which leads to the assumed pseudo-first-order decay of the solvent cation. Since the pulse lengths used were long compared to the 6 nsec rise and decay times of the pulse, Reaction 13 may be considered to begin at time \( t = 0 \), the beginning of the pulse, and to proceed at constant rate until \( t = p \), the end of the pulse. The concentration of neutral aromatic molecules in Reaction 10 remained effectively constant since, in all experiments, \([Ar] \gg [S^+]\). Also the aromatic cations formed are stable over the time range of interest here, i.e., the period of time when solvent cations are present.

This mechanism is described by the following set of differential equations:

\[
\begin{align*}
\frac{d[Ar^+]}{dt} &= k_{10}[Ar][S^+], & 0 < t < \infty \quad (VIII) \\
\frac{d[S^+]}{dt} &= k_{13} - (k_{10}[Ar] + k_{14})[S^+], & 0 < t < p \quad (IX) \\
&= - (k_{10}[Ar] + k_{14})[S^+], & p < t < \infty \quad (X)
\end{align*}
\]

The rate constant, \( k_{10} \), could be measured directly if one could observe the formation of \( Ar^+ \) after the end of the pulse. However, there was no detectable growth in optical density after the end of the pulse. Nevertheless, one can measure two quantities: the length of the pulse, \( p \), and an upper limit on the percentage, \( Q \), of the total
yield of \( \text{Ar}^+ \) which is formed after the end of the pulse. This is sufficient to determine a lower limit on the value of \( k_{10} \), which will be of interest.

In Appendix A the Equations VIII-X are integrated. It is shown that any growth after the pulse will have half-time of \( r = (\ln 2)/\kappa \) (where \( \kappa = k_{10}[\text{Ar}] + k_{11} \)) and the \( Q \) is given by

\[
Q = 100(1 - \exp(-\kappa p))/\kappa p
\]  

(11)

For a given pulse length, \( p \), one can calculate \( Q \) as a function of \( \kappa \).

Figure 8 shows a plot of \( Q \) versus \( \log \kappa \) for several pulse lengths. The corresponding values of \( r = (\ln 2)/\kappa \) are placed below the \( \log \kappa \) scale. Since the function is nonmonotonic, given \( p \) and \( Q \) (or an upper limit on \( Q \)), one can find \( \kappa \) (or a lower limit on \( \kappa \)) from this graph.

Figures 9 and 10 show the oscilloscope traces, taken with the faster detection system, when \( 2.0 \times 10^{-4} \) M solutions of biphenyl and \( \rho \)-terphenyl, respectively, were pulsed with the lamp shutter open and with the lamp shutter closed. The difference in these two traces gives the absorption after the pulse due to the aromatic cation. Comparison of the time profile of the emitted light with the time profile of the pulse current, which was measured electronically, shows that the duration of the emission gives an accurate measure of the pulse length. On the other hand, there are two factors which can prevent the accurate measure of \( Q \). First, if \( r \) is less than about 15 nsec, the end of the pulse becomes an ill-defined point due to the decay time of the pulse and the response time of the detection system. Second, if \( Q \) is very small, accurate measurement is not possible because of the poor signal to noise ratio. Actually these two problems
Figure 8: Plot of $Q$ versus $\log \kappa$ for pulse lengths (a) 140 nsec, (b) 90 nsec, (c) 50 nsec. $\tau = 0.693/\kappa$. $\%$
Figure 9: Formation of biphenyl cation. The oscilloscope picture shows the emission and absorption at 655 nm produced by a 90 ns, 600 m pulse in a $2.0 \times 10^{-4}$ M solution of biphenyl in 1,2-DCE at 25°C. This picture is inverted with respect to those in Figure 6.

Figure 10: Formation of para-terphenyl cation. The oscilloscope picture shows the emission and absorption at 52 nm produced by a 150 ns, 600 m pulse in a $2.0 \times 10^{-4}$ M solution of p-terphenyl in 1,2-DCE at -31°C. This picture is inverted with respect to those in Figure 6.
reduce to the same one since, for the pulse lengths used, it is clear
from the graph in Figure 8 that \( r < 15 \text{ nsec} \) implies \( Q < 20\% \). (The
signal to noise ratio can be improved by increasing the dose. How-
ever, this can be accomplished only by lengthening the pulse; but,
since \( k \) is fixed by the chemical system, this leads to a smaller \( Q \)
so that little advantage is gained.)

Figure 9 shows that \( Q < 30\% \) for a 90 nsec pulse. This gives
\( k > 3.5 \times 10^7 \text{ sec}^{-1} \) for biphenyl. The difference between the two
traces in Figure 10 shows that \( Q < 30\% \) for a 120 nsec pulse. This
gives \( k > 2.3 \times 10^7 \text{ sec}^{-1} \) for \( \text{p-terphenyl} \). Reaction 10, in terms of
the specific aromatic compounds becomes

\[
1,2-\text{DCE}^+ + \text{biphenyl} \rightarrow 1,2-\text{DCE} + \text{biphenyl}^+ \quad (15)
\]

\[
1,2-\text{DCE}^+ + \text{p-terphenyl} \rightarrow 1,2-\text{DCE} + \text{p-terphenyl}^+ \quad (16)
\]

Thus

\[
k_{15}[\text{biphenyl}] + k_{14} > 3.5 \times 10^7 \text{ sec}^{-1}
\]

\[
k_{16}[\text{p-terphenyl}] + k_{14} > 2.3 \times 10^7 \text{ sec}^{-1} \quad (XII)
\]

At some concentration of the aromatic compound, \([\text{Ar}]_2\), it will
be true that

\[
k_{10}[\text{Ar}]_2 = k_{14} \quad (XIII)
\]

and the rates of Reactions 10 and 14 will be equal. One half of the
solvent cations will react to form Ar\(^+\) and the yield of Ar\(^+\) will be
one half of the saturation yield, i.e., the yield at high \([\text{Ar}]\) where
essentially all S\(^+\) react with the aromatic compound. Substitution of
Equation XIII into Equation XII and rearrangement gives

\[
k_{15} > 3.5 \times 10^7 / ([\text{biphenyl}] + [\text{biphenyl}]_2)
\]

\[
k_{16} > 2.3 \times 10^7 / ([\text{terphenyl}] + [\text{terphenyl}]_2) \quad (XIV)
\]

Figure 7 gives the values of \([\text{biphenyl}]_2 = 9.5 \times 10^{-3} \text{ M}\)
\[ [\text{terphenyl}]_2 = 1.9 \times 10^{-3} \text{ M}. \]
The value of \([Ar]\) is the concentration of the aromatic compound used in the experiment where \(Q\) was measured and is equal to \(2 \times 10^{-4}\) M in both cases. Substitution into Equation XIV gives \(k_{15} > 3.0 \times 10^{10}\) M\(^{-1}\) sec\(^{-1}\) at \(25^\circ\text{C}\) and \(k_{16} > 1.1 \times 10^{10}\) M\(^{-1}\) sec\(^{-1}\) at \(-31^\circ\text{C}\). Substitution into Equation XIII gives \(k_{14} > 2 \times 10^7\) sec\(^{-1}\).

However, this last inequality is of little significance since Reaction 11 may represent several reactions, none of which are known with certainty.

For the assumed reaction mechanism, the probability that a given solvent ion will react to form an aromatic cation is \(k_{10}[Ar]/(k_{10}[Ar] + k_{14})\). The yield of \(Ar^+\), and hence \(D_p\), is proportional to this probability.

\[
D_p \propto \frac{k_{10}[Ar]}{k_{10}[Ar] + k_{14}} = \frac{x}{x + 1}
\]

where \(x = k_{10}[Ar]/k_{14}\). Thus

\[
\log D_p = \log(x/x + 1) + \text{constant}
\]

Also

\[
\log x = \log(k_{10}[Ar]/k_{14}) = \log[Ar] + \log(k_{10}/k_{14})
\]

Thus a plot of \(\log D_p\) versus \(\log[Ar]\), i.e., Figure 7, will be identical to a plot of \(\log(x/x + 1)\) versus \(\log x\) except for a constant displacement along the vertical axis and along the horizontal axis. The curves on Figure 7 are plots of \(\log(x/x + 1)\) versus \(\log x\) which have been displaced vertically and horizontally to give the best fit to the data.

The foregoing calculations and measurements are accurate if the decay of the solvent cations is pseudo-first-order in the absence of
an aromatic solute. If, on the other hand, reactions such as 11 have rates comparable to Reaction 10, the above conclusions will be only approximate. The quantity $k_{14}$ will no longer be a constant, but will increase with time as the concentration of counter ions builds up during the pulse. However, Figure 7 and Equation XIII still give an average value for $k_{14}$ relative to $k_{10[Ar]}$.

It is of interest to compare the lower limits for $k_{10}$ measured above with the rate constants one would expect if the rate were determined by the speed at which the reactants can diffuse together. In Appendix B these diffusion-controlled rate constants, $k_d(calc)$, are calculated for the reaction of biphenyl and $p$-terphenyl with the solvent cation. The values obtained are $9.8 \times 10^9 M^{-1} \text{sec}^{-1}$ for Reaction 15 at $25^\circ\text{C}$ and $3.5 \times 10^9 M^{-1} \text{sec}^{-1}$ for Reaction 16 at $-31^\circ\text{C}$.

However, these values are only approximate and probably more accurate values can be obtained by measuring the rate constant for several similar reactions which are thought to be diffusion controlled and making appropriate corrections for any differences in molecular size and in temperature. In the section on charge transfer, rate constants are measured for the reactions

$$\text{biphenyl}^+ + \text{pyrene} \rightarrow \text{biphenyl} + \text{pyrene}^+ \quad (17)$$

$$\text{$p$-terphenyl}^+ + \text{anthracone} \rightarrow \text{$p$-terphenyl} + \text{anthracone}^+ \quad (18)$$

The values obtained are $k_{17} = 9.9 \times 10^9 M^{-1} \text{sec}^{-1}$ at $24^\circ\text{C}$ and $k_{18} = 8.1 \times 10^9 M^{-1} \text{sec}^{-1}$ at $24^\circ\text{C}$. As is discussed in detail in that section, the rate of these reactions appears to be equal to the rate at which the reactants diffuse together. Theoretical predictions as well as measured rate constants for electron transfer between one
aromatic anion and another neutral aromatic molecule show that reactions of this type are diffusion controlled if $\Delta F^0$ for the reaction is less than about -0.4 ev. $\Delta F^0$ is the standard free energy of reaction and is about -1.4 and -1.2 ev for Reactions 17 and 18 respectively. These reactions are of the same type as Reaction 10, except that the reactant cation is an aromatic cation rather than a solvent cation.

Using Equation I from Appendix 3, one can correct these measured diffusion-controlled rate constants to the same temperature and molecular size as the calculated ones. If the biphenyl and p-terphenyl cations are assumed to have approximately the same size as the neutral molecules, then a correction must be made for the difference in size between 1,2-OC$_2^+$ and pyrene and anthracene respectively. Pyrene, which is planar and approximately elliptical, was taken to have an effective radius equal to the average of its two axes; anthracene was treated as a cylinder whose axis passed through the three aromatic rings and its radius taken to be that of a sphere of equal volume. $k_{18}$ was also corrected to -31°C.

This gave $1.1 \times 10^{-16}$ M$^{-1}$ sec$^{-1}$ ($= 1.2 \text{ k}_d$ (calc)) for Reaction 15 at 25°C and $3.3 \times 10^{-9}$ M$^{-1}$ sec$^{-1}$ ($= 0.35 \text{ k}_d$ (calc)) for Reaction 16 at -31°C. Comparison of these values with the measured lower limits for the rate constants $k_{15}$ and $k_{16}$ respectively shows that the formation of Ar$^+$ is faster than one would expect if the reactions were diffusion controlled. This implies an unusually high mobility of the positive charge. A possible explanation for this unusually high mobility of the positive charge may be the suggestion of previous investigators.
(11,15,21) that the positive hole can migrate through the solvent by a resonance charge transfer from a neutral to a positively ionized solvent molecule.

\[ 1,2-\text{DCE}^+ + 1,2-\text{DCE} \rightarrow 1,2-\text{DCE} + 1,2-\text{DCE}^+ \]  \hspace{1cm} (19)

Thus it would be possible for the positive charge to move through the solvent at a faster rate than the species \( 1,2-\text{DCE}^+ \) can diffuse through the solvent. This would cause the measured rate of aromatic cation formation to be higher than one would expect for a simple diffusion-controlled reaction. Shida and Hartill (11,13) have suggested a reaction comparable to Reaction 19 to explain their high yields of aromatic cations in polycrystalline \( \text{CCl}_4 \) and glassy butyl chloride, where the rate of diffusion of both the solvent cation and the aromatic molecule is very slow.

**DECAY OF THE AROMATIC CATION IN 1,2-DCB**

The aromatic cations observed in pulse irradiated, aerated 1,2-DCB solutions were found to decay over a period of tens of microseconds. The decay kinetics of the biphenyl cation were studied in detail in seeking to discover the reaction, or reactions, causing this decay.

As was already described in the Introduction, there is evidence that low energy electrons can react with benzy1 chloride in an alcohol (14), cyclohexane (9), or glassy 3-methyl pentane (8) solution by a dissociative attachment reaction:

\[ \text{e}^-_{(\text{sol})} + \text{BzCl} \rightarrow \text{Bz}^- + \text{Cl}^- \]  \hspace{1cm} (14)
where the electron is solvated in the case of the alcohol solvent. (The possible intermediate, \( \text{BrCl}^+ \), in Reaction 4, if it exists, has been shown \((44)\) to have a lifetime of less than \(5 \times 10^{-3} \text{ sec.}\))

This has led to the suggestion that after the secondary electrons—produced in the radiolysis of polycrystalline \( \text{CCl}_4 \) \((11,12)\) or chlorinated alkanes such as 1,2-DCE \((15)\)—have been degraded in energy, they may react with the solvent itself in a similar reaction. Thus in 1,2-DCE

\[
o^- + 1,2-\text{DCE} \rightarrow \text{C}_2\text{H}_4\text{Cl}^- + \text{Cl}^-
\]

In the experiments of Arai, et al. \((15)\) and Ueda \((21)\) the ratio \([1,2-\text{DCE}]/[\text{Ar}]\) was greater than \(10^2\) and Reaction 20 would compete overwhelmingly with electron attachment to the aromatic compounds if the rate constant for the latter reaction is not greater than \(k_{20}\). Since \(\text{Cl}^-\) would not transfer an electron to an aromatic molecule because of the higher electron affinity of the chlorine atom, this would explain why no aromatic anions were observed in 1,2-DCE and similar solvents.

If Reaction 20 does indeed occur, then a likely reaction for causing the disappearance of aromatic cations might be reaction with the chloride ion. If this is true, one should be able to increase the rate of the aromatic cation's decay by adding to the solution a chloride salt which will dissociate to give chloride ions. However, since 1,2-DCE is not highly polar, it is difficult to find a chloride salt which is sufficiently soluble and which dissociates to give free ions.
Tetraethylammonium chloride (Et₄Cl) was found to be soluble to
greater than 6.5 X 10⁻¹¹ M. When added to a 1.07 X 10⁻² M solution of
biphenyl, it greatly increased the rate of the biphenyl cation decay.
With [Et₄Cl] ≥ 1.86 X 10⁻⁵ M the decay of the biphenyl cation was
pseudo-first-order, i.e., a plot of log D versus time was linear, as
shown in Figure 11. (At [Et₄Cl] = 0.24 X 10⁻⁵ M the graphs showed
some curvature. This is to be expected since, as will be shown later,
this concentration of Et₄Cl is not much larger than the initial con­
centration of the biphenyl cation. Thus [Et₄Cl] will not remain
effectively constant throughout the course of the reaction and pseudo­
first-order kinetics can not be expected.) As shown in Appendix C,
the slope of the graph in Figure 11 gives the pseudo-first-order rate
constant for the decay of the biphenyl cation at a particular concen­
tration of Et₄Cl.

A plot of these observed pseudo-first-order rate constants, k',
(measured at 24°C and various concentrations of Et₄Cl) versus
[Et₄Cl] is linear over the range investigated (Figure 12). Thus

\[ k'_1 = k_a[Et₄Cl] + k_b \]  
(XVIII)

where \( k_a \) and \( k_b \) are constants. The first term on the right of
Equation XVIII is the pseudo-first-order rate constant for the reac­
tion of the biphenyl cation with Et₄Cl alone; \( k_b \) represents the con­
tribution, to the observed decay rate, of the other reactions of the
biphenyl cation, i.e., those reactions which occur in the absence of
Et₄Cl. The slope of the graph, \( k_a = 4 \times 10^{10} \, \text{M}^{-1} \, \text{sec}^{-1} \), gives the
bimolecular rate constant for the reaction of the biphenyl cation
with Et₄Cl.
Figure 11: Pseudo-first-order decay of biphenyl$^+$ in a 1,2-DCE solution containing $1.85 \times 10^{-5}$ M Et$_4$NCl following a 0.3 $\mu$sec pulse.
Figure 12: Plot of the pseudo-first-order rate constant, $k'$, for the decay of biphenyl$^+$ versus the concentration of Et$_2$NCl. $[\text{biphenyl}] = 1.06 \times 10^{-2}$ M, $T = 24^\circ C$. 
If the Et$_4$Cl exists in completely dissociated form in solution, $k_a$ will be the rate constant for the reaction of the biphenyl cation with chloride ion. However, since 1,2-DCE has a static dielectric constant of only 10.36 at 25°C (15), the Et$_4$Cl probably exists as free ions in equilibrium with associated ion pairs. Nevertheless, one would expect the rate at which a free chloride ion reacts with the biphenyl cation to be at least as great, if not greater, than the rate at which the associated ion pair reacts with it. This is because the ion pair is less mobile than free chloride; there is steric hindrance in the case of the ion pair because of the Et$_4$H$^+$ cation; and there is less coulombic attraction between biphenyl cation and the ion pair. Thus one expects the bimolecular rate constant for the reaction of biphenyl cations with free chloride ions to be given by: $k($biphenyl$^+$ + Cl$^-$) $\geq 4 \times 10^{10}$ M$^{-1}$ sec$^{-1}$.

Considering the large magnitude of this rate constant, if the concentration of the ions is high enough, one must consider the reaction

$$\text{biphenyl}^+ + \text{Cl}^- \rightarrow \text{products} \quad (21)$$

as a possible contributor to the observed decay of the biphenyl cation produced in irradiated 1,2-DCE solution. Other possible contributors to the decay include reaction with other radiolysis products, $R$, such as solvent derived free radicals,

$$\text{biphenyl}^+ + R \rightarrow \text{products} \quad (22)$$

and reaction with the solvent itself,

$$\text{biphenyl}^+ + 1,2\text{-DCE} \rightarrow \text{products} \quad (23)$$
One must also consider the possibility of reaction with impurities which may be introduced either with the solvent or with the biphenyl, especially if $[\text{biphenyl}]$ is rather large.

\[ \text{biphenyl}^+ + \text{I} \rightarrow \text{products} \]  \hspace{1cm} (2h)

Reactions such as 21 and 22 of the biphenyl cation with other radiolysis products that are produced with yields comparable to that of $\text{biphenyl}^+$ will cause the decay of $\text{biphenyl}^+$ to appear second order in nature, i.e., a plot of $1/\theta$ versus $t$ will be linear (see Appendix C). Reactions such as 23 and 24 (if $[\text{I}]$ is greater than about $5 \times 10^{-5}$ M) will cause the decay of $\text{biphenyl}^+$ to appear pseudo-first-order since the concentration of the second reactant will remain effectively constant during the course of the reaction. If several of the above reactions are occurring with comparable rates, then the observed decay may be of mixed order.

Alternatively, if $\text{biphenyl}^+$ is reacting with one other radiolysis product, $R$, which is produced in somewhat higher yield than the biphenyl cation, a mixed first- and second-order decay will also be observed, for the following reason. Suppose that the concentrations at the end of the pulse are given by $[\text{biphenyl}^+]_p$ and $[R]_p$ and that

\[ [R]_p = [\text{biphenyl}^+]_p + C \]  \hspace{1cm} (XIX)

where $C$ is a positive constant. The rate of the reaction of $\text{biphenyl}^+$ with $R$ will be given by

\[ -d[\text{biphenyl}^+]/dt = k_{22}[R][\text{biphenyl}^+] \]  \hspace{1cm} (XX)

If the only important reaction of $\text{biphenyl}^+$ and of $R$ is their reaction with each other, then at all times it will be true that

\[ [R] = [\text{biphenyl}^+] + C \]  \hspace{1cm} (XXI)
and this relation can be substituted into Equation XX to give

\[-d[biphenyl^+] / dt = k_{22}[biphenyl^+]^2 + k_{22}C[biphenyl^+] \]  (XXII)

Thus the decay of the biphenyl cation will appear to be mixed first- and second-order. The observed second order rate constant, \( k_{22} \), will be equal to the bimolecular rate constant for the reaction and should be independent of dose. The observed first order rate constant will be equal to \( k_{22}C \) and should be proportional to the dose if the yields of biphenyl\(^+\) and \( R \) are proportional to dose.

The decay of the 690 nm band of the biphenyl cation in aerated \( 1,2\)-DCB solution was found to be mixed order, i.e., it did not give either a good first- or second-order plot. Figure 13 is an oscilloscope picture showing the decay on two time scales. (No aerated biphenyl solutions were investigated with the faster detector. However, argon saturated, \( 2 \times 10^{-2} \) M biphenyl solutions showed no unusually fast decay during the first 100 nscc following the pulse, such as has been observed for aromatic ions in some solvents (2,33).)

In Appendix C it is shown that if the overall decay of an absorbing species is effectively a mixed first- and second-order decay, then a plot of \( 1/D_t + \theta \) versus \( 1/D_t \), with \( \theta \) a positive constant, will be linear. The effective first-order rate constant, \( k_f \), will be given by

\[ k_f = (\ln \sigma) / \theta \]  (XXIII)

and the effective second order rate constant, \( k_s \), will be given by

\[ k_s = e \sigma \ln \sigma \frac{1}{\theta(\sigma - 1)} \]  (XXIV)

where \( \sigma \) and \( \theta \) are the slope and the vertical-axis intercept of the
Figure 13: Decay of the absorption at 690 nm in an aerated 1,2-DCE solution of 1.01 × 10^{-2} M biphenyl following a 0.6 μsec, 325 mA pulse. The temperature is 21°C. The sweep speed of the upper trace is 0.5 μsec per major division. The lower trace has a sweep speed of 5.0 μsec per major division and is expanded vertically by a factor of two.
graph, respectively. Figure 14 is such a plot of the data from Figure 13. The plot shows good linearity over greater than 90\% of the reaction. Similar plots were obtained for decays measured over a range of doses.

The dose was proportional to the pulse length so that the relative dose could be measured from the duration of the linear growth portion of the upper trace (see Figure 13). Figures 15 and 16 show values of $k_f$ and $k_s/d_{690}^{biphenyl^+}$, obtained from the graphs using Equations (XXIII) and (XXIV) respectively, plotted versus the relative dose. The value of $k_f$ is proportional to the dose over a greater than five-fold range. The value of $k_s/d_{690}^{biphenyl^+}$ is independent of dose over the same range. At lower doses the determination of the intercept, $l$, involves a longer extrapolation, which accounts for the somewhat greater scatter in the points at that end of the graph.

This observed behavior of the decay of biphenyl$^+$ is just what was predicted above for reaction of the biphenyl cation with one other radiolysis product, R, which has a somewhat higher yield than the biphenyl cation. This is provided that $[\text{biphenyl}^+]_p$ and $[R]_p$, or at least their difference, are proportional to the dose. Figure 17 shows that $[\text{biphenyl}^+]_p$ is proportional to the dose, since $D_p \propto [\text{biphenyl}^+]_p$; it is reasonable to assume that $[R]_p$ will also be proportional to the dose.

If, as these results suggest, the decay of biphenyl$^+$ is due primarily to one reaction, it will be of interest to determine $k_s$, the bimolecular rate constant for this reaction. To do this it is
Figure 11: Test of the data from Figure 13 for effective mixed first- and second-order decay of biphenyl\(^+\) following a 0.6 \(\mu\)sec pulse.
Figure 15: Plot of the effective first-order rate constant for biphenyl$^+$ decay versus pulse length. [biphenyl] = 1.01$ \times$ 10$^{-2}$ M, $T = 24^\circ$C.
Figure 16: Plot of $k_g/d_{690}^{690}$ versus pulse length. [biphenyl] = $1.01 \times 10^{-2} M$, $T = 24^\circ C$. 
Figure 17: Plot of the optical density at 690 nm at the end of the pulse versus pulse length. [biphenyl] = 1.01 \times 10^{-2} M, T = 24°C.
necessary to know $\epsilon_{\text{biphenyl}^+}$. This extinction coefficient is not known; however, it can be estimated by the following experiment.

It has been found (16,42) that, when anthracene is dissolved in a solution of $\text{BF}_3\cdot\text{H}_2\text{O}$ and $\text{O}_2$ in $\text{CF}_3\text{CO}_2\text{H}$, some of the anthracene is converted to anthracene$^+$ and the rest to anthracene$^{1+}$. The overlapping absorption spectra of the two species are observed. However, the absorption spectrum of anthracene$^{1+}$ is known from solutions of anthracene in $\text{O}_2$-free HF. Thus, the composite spectrum can be corrected to give the spectrum one would obtain if all the anthracene were converted to the anthracene cation. This corrected spectrum gives an extinction coefficient of approximately $9.5 \times 10^3$ $\text{M}^{-1}\text{cm}^{-1}$ for the peak of the 725 nm band of anthracene$^+$.  

1,2-DCB solutions of biphenyl and of anthracene, each $1.02 \times 10^{-2}$ M, were irradiated with equal pulses. This concentration was chosen since it gives the highest yield of anthracene cation, there being a slight fall off in yield at higher concentration. This fact, together with consideration of the curve in Figure 7, shows that in both solutions nearly all of the solvent cations will be converted to the respective aromatic cations. Thus, since the dose is the same, the yield of aromatic cations will be approximately equal in the two solutions. Then

$$\frac{D_{\text{biphenyl}}^{690}}{D_{\text{anthracene}}^{725}} = \frac{\epsilon_{\text{biphenyl}^+}^{690}}{\epsilon_{\text{anth}^{1+}}^{725}}$$

The optical densities were measured by extrapolating to the middle of the pulse. This corrected for the slight amount of the total yield
of cations that decayed during the pulse. The measured ratio was 1.13. Multiplying this by the approximate value of $\text{anth}^+ \times 690$ gives $c_{\text{biphenyl}^+} = 1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

Using this very approximate value for the extinction coefficient, one obtains from the above measurement of $k_g/d_e690$ that $k_g = 1.1 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}$.

For biphenyl$^+$ reacting with radiolysis product, $R$, whose concentration at the end of the pulse is $G$ greater than that of the biphenyl cation, Equation XXII shows that $k_f$ is actually the product of $k_g$ and $G$. Combining this with the fact that $[\text{biphenyl}^+]_p = D_p/\varepsilon d$ gives

$$C = k_f (XXVI)$$

The three quantities $k_f$, $(k_g/\varepsilon d)$, and $D_p$ are directly measurable from the data, i.e., they do not depend on the estimate of $690$ biphenyl$^+$. The ratio on the left will be independent of the dose since $k_f$ and $D_p$ are proportional to the dose and $(k_g/\varepsilon d)$ is independent of it. Averaging over all doses gives $C/[\text{biphenyl}^+]_p = 0.22$.

Thus the data is consistent with the interpretation that the dominant decay mode of biphenyl$^+$ is its reaction with another radiolysis product whose yield is about 22% higher than that of biphenyl$^+$ and that the bimolecular rate constant for this reaction is very approximately given by $10^{11} \text{ M}^{-1} \text{ sec}^{-1}$. Since the counter ion is thought to be chloride, and, as shown above, the reaction of chloride with biphenyl$^+$ should have a rate constant $\geq 4 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, it would appear very likely that the radiolysis product which causes the
decay of biphenyl$^+$ is just the counter ion, Cl$^-$. Furthermore it is quite possible that in a 10$^{-2}$ M biphenyl solution 18% of the positive charges are not scavenged by biphenyl, while essentially all of the negative charges exist as Cl$^-$. Thus [Cl$^-$]$_p$ could be somewhat greater than [biphenyl$^+$]$_p$, i.e., C = 0.22.

The above interpretation is consistent with the data and satisfactorily explains the observed facts. However, it is possible that some combination of Reactions 21 through 24 might lead to an apparent mixed first- and second-order decay. If a combination of reactions is occurring, the measured value of $k_s$ will reflect the rates of reactions of biphenyl$^+$ with other species of comparable concentration, and $k_{21}$ may be less than the measured $k_s = 10^{11}$ M$^{-1}$ sec$^{-1}$. The value of $k_f$ will reflect the combined rate of pseudo-first-order reactions plus terms involving concentration differences, such as C above. However, if there are important pseudo-first-order reactions such as 23 or 24 occurring, it is hard to explain why $k_f$ extrapolates to zero at zero dose.

In support of the foregoing interpretation that biphenyl$^+$ decays primarily by reaction with Cl$^-$ is the fact that the 965 nm absorption band of the p-terphenyl cation, in aerated 1,2-DCE solution, decays with an approximately second-order rate.

Several other investigators (15,21) have observed the decay of biphenyl$^+$ in irradiated 1,2-DCE. Arad, et al. (15) found a mixed first- and second-order decay of biphenyl$^+$ in degassed 1,2-DCE solution. On the other hand Ueda (21) reports that the decay of biphenyl$^+$,
and also of trans-stilbene\textsuperscript{+}, in degassed 1,2-DCE solution is first-order or pseudo-first-order.

These results can not be compared directly with the present work since air, which was present in the solutions investigated in this study, has been shown (15) to have the effect of increasing slightly the lifetime of biphenyl\textsuperscript{+} in irradiated solutions. Possibly oxygen scavenges certain radiolysis products which would otherwise react with the aromatic cation.

Ueda (21) explains his findings by suggesting that 1,2-DCE\textsuperscript{-} does not dissociate and that the negative charge moves rapidly through the solvent in a manner similar to that suggested above for the positive hole's migration. Thus Ar\textsuperscript{+} and 1,2-DCE\textsuperscript{-} encounter each other very quickly and exist for some time as an ion pair because of some energy barrier to neutralization. The barrier is not high and the pairs eventually self-neutralize in a first-order process. He measures activation energies of 3.62 and 1.27 kcal/mole for the disappearance of biphenyl\textsuperscript{+} and trans-stilbene\textsuperscript{+}, respectively, in 1,1-dichloroethane. These activation energies presumably show the height of the barriers to neutralization.

However, an alternative explanation for Ueda's findings might be that there was a high enough concentration of radiolysis products (since O\textsubscript{2} was absent) and/or of impurities to cause a pseudo-first-order decay of Ar\textsuperscript{+}. (His reported decay rate of biphenyl\textsuperscript{+} is significantly faster at long times than observed in this work.) If such reactions occur with diffusion-controlled rates, they will have an apparent activation energy due to the temperature dependence of
viscosity (see Appendix B). In 1,2-DCE, for example, this activation energy will be about 2 kcal/mole.

The approximate value of $E_{\text{biphenyl}}$ measured above can be used to calculate $[\text{biphenyl}^+]_p$, the concentration of biphenyl cations at the end of the pulse, from $P_p$. Thus with $[\text{biphenyl}] = 10^{-2} \text{ M}$ and a 0.3 μsec, 325 nm pulse, $[\text{biphenyl}^+]_p \approx 2.1 \times 10^{-6} \text{ M}$. Figure 17 shows that $[\text{biphenyl}^+]_p$ is proportional to pulse length up to at least a 0.5 μsec pulse.

A reaction not yet considered, which may lead to the decay of certain aromatic cations in solution, is

$$\text{Ar}^+ + \text{Ar} \rightarrow (\text{Ar}_2)^+$$

(25)

There is evidence from c.s.r. studies of aromatic cations produced by chemical oxidation (66,67) that naphthalene cations and anthracene cations react in this way. Furthermore, the observations indicate that the dimer cations form with the planes of the aromatic molecules parallel. Thus the cations of biphenyl and of p-terphenyl would not be expected to react in this way to any appreciable extent.

Reaction 25 will proceed until an equilibrium is established. Badger and Brocklehurst have estimated equilibrium constants for a number of aromatic compounds (68). If $[\text{Ar}]$ is sufficiently large the reaction may be very fast and the equilibrium shifted far to the right. Thus when $2 \times 10^{-2} \text{ M}$ naphthalene in 1,2-DCE is irradiated with a 1 μsec pulse, the absorption spectrum observed after the pulse is not the spectrum expected for naphthalene$^+$ (69) but does resemble a spectrum attributed to $(\text{naphthalenog})^+$ by Badger, et al. (59). Reaction 25 may also explain the slight fall off in yield of anthracene$^+$ above
a certain concentration of anthracone.

**Charge Transfer Reactions**

Arai, et al. (15) observed that, when a 1,2-DCB solution of two aromatic compounds, $A_{Ra}$ and $A_{Rb}$, was irradiated, the reaction

$$A_{Ra}^+ + A_{Rb} \rightarrow A_{Ra} + A_{Rb}^+$$

occurred for certain aromatic pairs for which the ionization potential of $A_{Ra}$ was greater than that of $A_{Rb}$. Since rate constants for this type of reaction are unknown, a number of pairs were investigated in this study to determine the rate of the charge transfer reaction.

Ideal conditions for measuring such a rate constant would be:

- formation of $A_{Ra}^+$ essentially complete at the end of the pulse; high, easily observable $[A_{Ra}^+]$ and low $[A_{Rb}^+]$ at the end of the pulse;
- $[A_{Rb}] \gg [A_{Ra}]$ so that the reaction would be pseudo-first-order;
- Reaction 26 the only reaction involving $A_{Ra}^+$ and $A_{Rb}^+$; and non-overlapping absorption bands of $A_{Ra}^+$ and $A_{Rb}^+$ so that the decay of $A_{Ra}^+$ and the growth of $A_{Rb}^+$ could be monitored independently.

Most of these conditions could be achieved for selected pairs of aromatic compounds using the pulse radiolysis techniques of this study. The usual procedure, for measuring rate constants that were in the $10^9 - 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ range, was to prepare an aerated 1,2-DCB solution with $[A_{Ra}] \geq 10^{-2} \text{ M}$ and $1 \times 10^{-5} \leq [A_{Rb}] \leq 5 \times 10^{-4} \text{ M}$, where $A_{Ra}$ is the aromatic compound with the larger ionization potential; and to irradiate it with a 0.2 - 0.3 usec pulse. If the rate constant for $3^+ + A_{Ra}$ is comparable for the two aromatic compounds, these
concentrations greatly favor the formation of $\text{Ar}_a^+$ over $\text{Ar}_b^+$. (The exact value of $[\text{Ar}_b^+]$ at the end of the pulse is not important, so long as it is relatively small.) $[\text{Ar}_b^+]$ is large enough to make the reaction pseudo-first-order but low enough so that the half-time of the reaction is greater than about 0.2 µsec. Thus most of the reaction occurs after the pulse and is slow enough for the detection system to follow accurately.

As shown in a previous section, the formation of $\text{Ar}_a^+$ is very fast and is essentially complete at the end of the electron pulse. On the other hand, it was shown in the section on aromatic cation decay that Reaction 26 will not be the only reaction involving $\text{Ar}_a^+$ and $\text{Ar}_b^+$. Both cations will be reacting with the counter ion during the same time. Nevertheless, the higher $[\text{Ar}_b^+]$ is made, the faster Reaction 26 will proceed and the effects of other reactions on the kinetics will be minimized.

Whether or not the absorption spectra of the two cations have non-overlapping bands will depend, of course, on the aromatic pair chosen. However, as will be explained later, the kinetics of the reaction can still be followed even if the spectral bands do overlap.

Two types of observations will give evidence that Reaction 26 does take place for a given pair of aromatic compounds, $\text{Ar}_a$ and $\text{Ar}_b$, where $\text{Ar}_a$ has the higher ionization potential. One observation is that, at fixed $[\text{Ar}_a^+]$, the rate of decay of $\text{Ar}_a^+$ increases with increasing $[\text{Ar}_b^+]$. This indicates that $\text{Ar}_b$ reacts in some way with $\text{Ar}_a^+$ to cause its decay, but the nature of the reaction is undetermined. The other type of observation, which indicates the nature of the
reaction, is that the decay rate of an absorption band of Ar$_a^+$ is matched by the growth rate of an absorption band of Ar$_b^+$.

If these two absorption bands overlap in some wavelength region, one will observe either a net decay or net growth in optical density after the pulse depending on which of the cations absorbs more strongly at the particular wavelength observed. If a point exists where $\varepsilon(\lambda)$ (Ar$_a^+$) = $\varepsilon(\lambda)$ (Ar$_b^+$), the absorption will show no change with time since each Ar$_a^+$ lost is replaced by an Ar$_b^+$ and the two cations absorb equally well. (There will be a slow decay in the absorption because both cations are reacting concurrently with the counter ion. However, the rate of these reactions will be negligibly slow compared to Reaction 26 if [Ar$_b$] is high enough.) Thus if one finds a wavelength, $\lambda_1$, between the band peaks of Ar$_a^+$ and Ar$_b^+$ such that on one side of $\lambda_1$ there is a net decay of optical density and on the other side a net growth, with no change at $\lambda_1$, this is good evidence that Ar$_a^+$ decays and Ar$_b^+$ forms with the same rate. Detailed analysis of rate curves is not needed.

The method used for determining the rate constant for Reaction 26 was to analyze the rate of Ar$_a^+$ decay at various concentrations of Ar$_b$. The change of this decay rate with [Ar$_b$] gave the rate constant, as will be seen. (The formation curve of Ar$_b^+$ was difficult to analyze because of the concurrent slower reaction with the counter ion. Furthermore, the technique used for separating overlapping absorptions gives only a quantity proportional to [Ar$_a^+$].)

In the pairs of aromatic compounds investigated here, Ar$_a$, i.e., the species whose cation was observed to determine the rate constant,
was either biphenyl or para-terphenyl. As already discussed, the formation, in irradiated 1,2-DCE, of the cations of these two compounds and the absorption spectra of the cations have been well substantiated. Furthermore, as pointed out previously, with these two compounds there is less likelihood than with planar aromatic compounds that Ar^+ will react with Ar^+ to give a dimer cation. The pairs which have been investigated will be considered individually.

**Para-terphenyl - Anthracene**

This was the most ideal of the pairs investigated, there being the least problem with spectral overlap. When a solution of para-terphenyl alone (2.5 X 10^-2 M) was irradiated with a 0.2 μsec pulse, the p-terphenyl cation was observed at 965 nm and had a decay whose initial half-life was about 9 μsec. The absorption at 725 nm, where the optical density was about 15% of that at 965 nm, showed the same decay. When anthracene was added (5.5 X 10^-5 - 6.7 X 10^-4 M), the decay rate at 965 nm was greatly increased and the absorption at 725 nm (the peak of the anthracene* band) now showed a growth, following the end of the pulse, whose rate corresponded to the decay rate at 965 nm. A point, λ₁, of non-changing absorption was observed at approximately 760 nm in the solution with [anthracene] = 6.7 X 10^-4 M. The foregoing observations give good evidence for the reaction

\[
p^-\text{terphenyl}^+ + \text{anthracene} \rightarrow p^-\text{terphenyl} + \text{anthracene}^+ \quad (27)
\]

The rate of this reaction was measured in solutions with \([p^-\text{terphenyl}] = 9.8 X 10^{-3} \text{ M}\) and with [anthracene] varied from
$3.93 \times 10^{-5}$ to $3.59 \times 10^{-4}$ using a 0.2 μsec pulse. The absorption at 965 nm decayed with a pseudo-first-order rate to about 1% absorption, indicating that the overlapping absorption from anthracene was very small at this wavelength. Figure 18 shows plots of log D (with the 1% absorption subtracted out) versus t for two concentrations of anthracene. The slopes of such graphs give $k_{27}^1$, the pseudo-first-order rate constant for the decay of $p$-terphenyl at that particular concentration of anthracene (see Appendix C). Figure 19 shows a plot of $k_{27}^1$, measured in this way, versus \([\text{anthracene}]\). The graph shows that $k_{27}^1$ varies linearly with anthracene concentration over nearly a tenfold range of \([\text{anthracene}]\). From the line drawn through the points

$$k_{27}^1 = (8.1 \times 10^7[\text{anthracene}] + 1.4 \times 10^5) \text{ sec}^{-1} \quad (XXVII)$$

\[\text{BIPHENYL} \rightarrow \text{PARA-TERPHENYL}\]

When a $2.98 \times 10^{-2}$ M solution of biphenyl alone was irradiated with a 0.1 μsec pulse, the 690 nm absorption band of biphenyl was observed. It decayed with an initial half-life of about 1.6 μsec. The absorption at 965 nm was very weak and showed only decay after the pulse. When \(p\)-terphenyl was added ($0.55 \times 10^{-4} - 5.86 \times 10^{-4}$ M) the decay rate of the 690 nm band increased and a corresponding growth was observed at 965 nm (the absorption peak of \(p\)-terphenyl). A point, $\lambda_1$, of non-changing absorption was observed near 765 nm in a solution containing $5.86 \times 10^{-4}$ M \(p\)-terphenyl. These facts give evidence for the reaction

biphenyl$^+ + p$-terphenyl $\rightarrow$ biphenyl + $p$-terphenyl$^+$ \quad (28)
Figure 18: Pseudo-first-order decay of p-terphenyl$^+$ at two concentrations of anthracene, O, $3.92 \times 10^{-5}$ M; O, $2.78 \times 10^{-4}$ M. $[\text{p-terphenyl}] = 9.0 \times 10^{-3}$ M in both solutions. D(corrected) = $\log \left( \frac{I_0 - c}{I_t} \right)$, where $c \approx 0.01 \times I_0$ and corrects for what appears to be a slight absorption due to anthracene$^+$. 
Flours 19: Plot of the pseudo-first-order rate constant, $k_{27}$, for the decay of p-terphenyl$^+$ versus the concentration of anthracene. $[p$-terphenyl$]$ = $2.8 \times 10^{-3}$ M, $T = 24^\circ C$. $[\text{]}$, average $k^1$ from n individual rate curves; $[]$, range of the n points when outside $\square$; $O$, $k_p$, as defined on page 82. 

Figure 19: Plot of the pseudo-first-order rate constant, $k_{27}$, for the decay of p-terphenyl$^+$ versus the concentration of anthracene. $[p$-terphenyl$]$ = $2.8 \times 10^{-3}$ M, $T = 24^\circ C$. $[\text{]}$, average $k^1$ from n individual rate curves; $[]$, range of the n points when outside $\square$; $O$, $k_p$, as defined on page 82.
The rate of this reaction was studied, using a 0.3 μsec pulse, by monitoring the decay of the absorption at 685 nm. However, since \( p \)-terphenyl\(^+\) absorbs somewhat at this wavelength (the 965 nm band of \( p \)-terphenyl\(^+\) has a long tail into the visible region) the absorption did not decay to zero, but rather to a plateau, as seen in Figure 20a. Figure 20b shows the absorption at 965 nm produced by a subsequent pulse in the same solution. Clearly Reaction 28 is occurring during the first part of the trace and is essentially complete by the middle of the picture, \( t = q \). The absorption after this point should be due entirely to the product, \( p \)-terphenyl\(^+\), which is slowly decaying due to reaction with the counter ion.

If this is true, then it is shown in Appendix D that plots of \( \log D_t^{685} \) and \( \log D_t^{965} \) versus time will be superimposable, in the region \( t \geq q \), by a vertical displacement. The amount of displacement required gives the value of \( \log(\epsilon_{685}^{p\text{-terphenyl}^+}/\epsilon_{965}^{p\text{-terphenyl}^+}) \). The zero of time is taken as the end of the pulse in each graph. Figure 21 shows superimposed plots of the data from Figure 20.

Furthermore, it is shown in Appendix D that at all times after the pulse
\[
D'_t = \epsilon'[\text{biphenyl}^+]_t = \frac{D_t^{685} - \left(\frac{\epsilon_{685}^{p\text{-terphenyl}^+}}{\epsilon_{965}^{p\text{-terphenyl}^+}}\right)D_t^{965}}{(XXVIII)}
\]
where \( \epsilon' \) is a constant. \( D_t^{685} \) and \( D_t^{965} \) are measurable from the traces in Figure 20; the ratio of extinction coefficients is obtained from Figure 21 as described above. Thus one can measure a quantity, \( D' \), proportional to \( [\text{biphenyl}^+]_t \). This is sufficient for the study of pseudo-first-order kinetics, as is clear from Appendix C, since the
Figure 20: Oscilloscope traces following irradiation with a 0.3 μsec pulse of a solution containing $3.0 \times 10^{-2}$ M biphenyl and $2.80 \times 10^{-4}$ M p-terphenyl at 25°C. The wavelength observed is (a) 685 nm; (b) 965 nm.
Figure 21: Superposition of the data from Figure 20 for $t \geq 2.5\ \mu\text{sec}$. $\Delta$, $\lambda = 685\ \text{nm}$, $a = 1$; $O$, $\lambda = 965\ \text{nm}$, $a = 0.0867$. ($a = \epsilon_{605}^{\text{p-torphenyl}^{+}}/\epsilon_{965}^{\text{p-torphenyl}^{+}}$)
proportionality constant cancels out.

The procedure used here was to photograph several traces at 665 nm and one at 965 nm for each concentration of p-terphenyl. The entire measurement process described above was carried out individually for each of the 665 nm pictures. Thus errors were not introduced because of small fluctuations in dose (see Appendix D).

Figure 22 shows plots of log D' versus t for two concentrations of p-terphenyl. The biphenyl cation is found to decay by a pseudo-first-order rate law. The slopes of such graphs give the pseudo-first-order rate constants, k', for biphenyl decay at particular concentrations of p-terphenyl. Figure 23 is a plot of k' versus \([p\text{-terphenyl}]\). k' is found to vary linearly with \([p\text{-terphenyl}]\) over a nearly eight-fold range of this concentration. The graph gives

\[
k'_{28} = (5.1 \times 10^2[p\text{-terphenyl}] + 5.5 \times 10^5) \text{ sec}^{-1}
\]

BIPHENYL - PYRENENE

Observations of an irradiated solution of biphenvy1 alone have been considered in connection with the preceding pair. If pyrene was added to a 2.12 \times 10^{-2} \text{ M} biphenvy1 solution, the decay rate of the 690 nm band was increased. A point, \(\lambda_1\), of non-changing absorption was observed around 785 nm in a solution having [pyrene] = 1.96 \times 10^{-4} \text{ M}. Above this wavelength the absorption showed growth, rather than decay, immediately after the pulse. This evidence strongly suggests the occurrence of the reaction

\[
\text{biphenvy1}^+ + \text{pyrene} \rightarrow \text{biphenvy1} + \text{pyrene}^+
\]
Figure 22: Pseudo-first-order decay of biphenyl$^+$ at two concentrations of $p$-terphenyl, $O$, $5.53 \times 10^{-5}$ M; $\Phi$, $3.59 \times 10^{-4}$ M. [biphenyl] = $3.0 \times 10^{-2}$ M in both solutions.
Figure 23: Plot of the pseudo-first-order rate constant, $k_{2g}$, for the decay of biphenyl$^+$ versus the concentration of p-terphenyl. [biphenyl] = 3.0 X $10^{-2}$ M, $T = 25^\circ$C. $\overline{n}$, average $k^i$ from $n$ individual rate curves; $I$, range of the $n$ points when outside $\Box$; $O$, $k_p$, as defined on page 62.
The rate of this reaction was studied by using a 0.3 μsec pulse and again observing the decay of biphenyl• at 685 nm. As with the preceding pair, the signal did not decay to zero because of the overlapping absorption of pyrene•. Figure 24 shows the absorption at 685 nm and at 780 nm. Since ε_{biphenyl•} > ε_{pyrene•} at both of these wavelengths, an overall decay is observed. Nevertheless, since the ratio of the two extinction coefficients is different at the two wavelengths, the method for separating overlapping absorptions described in Appendix D is still applicable. Thus one can use the same method of data analysis as with the preceding pair. Figure 25 shows plots of log D^{685} and log D^{780} versus t which have been displaced vertically so as to coincide where t > q. The amount of displacement gives log(ε_{685}^{pyrene•}/ε_{780}^{pyrene•}) and hence one can measure D_{t} α [biphenyl•]_{t}. Figure 26 shows a plot of log D' versus t (t = 0 at the end of the pulse) for two concentrations of pyrene. For 0.895 X 10^{-3} ≤ [pyrene] ≤ 3.25 X 10^{-3} M, the biphenyl cation was found to decay by a pseudo-first-order rate law. At [pyrene] = 0.407 X 10^{-3} M, the decay of biphenyl• showed a small second order component. This is not unexpected, however, since at this low concentration of pyrene the reaction of biphenyl• with the counter ion will compete significantly with the charge transfer reaction.

From the slope of graphs such as in Figure 26 one obtains the pseudo-first-order rate constants for the decay of biphenyl• at particular concentrations of pyrene. Figure 27 shows a plot of k' versus [pyrene]. From this graph...
Figure 2: Oscilloscope traces following irradiation with a 0.3 μsec pulse of a solution containing $2.1 \times 10^{-2}$ M biphenyl and $8.89 \times 10^{-5}$ M pyrene at 24°C. The wavelength observed is (a) 685 nm; (b) 780 nm.
Figure 25: Superposition of the data from Figure 24 for $t \geq 3.5 \mu$sec. ▲, $\lambda = 685$ nm, $a = 1$; ○, $\lambda = 780$ nm, $a = 0.761$. $\frac{a_{\text{pyrene}^+/\text{pyrene}^+}}{685}$
Figure 26: Pseudo-first-order decay of biphenyl$^+$ at two concentrations of pyrene, O, $8.89 \times 10^{-3}$ M; O, $3.25 \times 10^{-4}$ M. [biphenyl] = $2.1 \times 10^{-4}$ M in both solutions.
Figure 27: Plot of the pseudo-first-order rate constant, $k_{29}^p$, for the decay of biphenyl$^+$ versus the concentration of pyrene. [biphenyl] = $2.1 \times 10^{-2}$ M, $T = 24^\circ$C. [5], average $k'$ from $n$ individual rate curves; $\bar{I}$, range of the $n$ points when outside O, $k_p$, as defined on page 82.
For each of the three reactions investigated above it was found that the pseudo-first-order rate constant, \( k' \), for the decay of Ar\(_a^+\) was a linear function of [Ar\(_b\)] over the range investigated.

\[
k' = k_a[Ar_b] + k_b
\]

(XXI)

where \( k_a \) and \( k_b \) are constants. The first term on the right, \( k_a[Ar_b] \), shows the effect on the overall decay rate of Ar\(_a^+\) caused by the addition of Ar\(_b\) to the solution. Now the pseudo-first-order rate constant for the transfer reaction (Reaction 26) is \( k_{26}[Ar_b] \), where \( k_{26} \) is the bimolecular rate constant for the charge transfer reaction. Thus, assuming that the only effect of the presence of Ar\(_b\) on the decay of Ar\(_a^+\) is that of Reaction 26, the measured values, \( k_{26} \), give the bimolecular rate constants, \( k_{26} \).

This conclusion can also be derived in the following way. The decay of Ar\(_a^+\) is given by

\[
- \frac{d[Ar_a^+]}{dt} = \left\{k_{26}[Ar_b] + k_t\right\}[Ar_a^+]
\]

(XXXII)

where \( k_t[Ar_a^+] \) is the rate of Ar\(_a^+\) decay in the absence of Ar\(_b\), thought to be due to reaction with the counter ion. Since the decay of Ar\(_a^+\) is not pseudo-first-order in the absence of Ar\(_b\), as shown in the previous section, \( k_t \) is a decreasing function of time. However, if [Ar\(_b\)] is made large enough, \( k_t \) will be nearly constant during the time over which the decay of Ar\(_a^+\) is measured and may be approximated by \( k_b \), the value of \( k_t \) at the end of the pulse. The accuracy of this approximation will increase with increasing [Ar\(_b\)]. Thus Equation XXXII becomes approximately
This predicts a pseudo-first-order decay of $\text{Ar}_d^+$ with $k' = k_{26}[\text{Ar}_b] + k_p$. A pseudo-first-order decay is actually observed with $k' = k_a[\text{Ar}_b] + k_p$, as shown above. Thus $k_a = k_{26}$, where $k_a$ is the measured quantity and $k_{26}$ is the bimolecular rate constant for the charge transfer reaction. Also $k_b = k_p$, where $k_p$ is the rate of decay of $\ln[\text{Ar}_b^+]$ at the end of the pulse in the absence of any $\text{Ar}_b$ (Equation XXXIV). One can measure $k_p$ approximately by plotting $\ln J$ versus $t$ for a solution with $[\text{Ar}_b] = 0$ and then taking the initial slope (i.e., at the end of the pulse). This value should approximately equal the vertical-axis intercept, $k_b$, for the same pair. Measured values of $k_p$ are plotted on the graphs in Figures 19, 23, and 27 and are in satisfactory agreement with the vertical-axis intercepts of the straight lines drawn through the other points.

One must consider the possibility that, while Reaction 26 is occurring, the reverse reaction may also be occurring. In particular, consideration must be given whether this will effect the value one measures for the rate constant of the forward reaction.

If the reverse of Reaction 26 is significant, charge transfer will take place after the pulse until equilibrium concentrations of $\text{Ar}_d^+$ and $\text{Ar}_b^+$ are achieved. Beyond this point both aromatic cations will decay away by reaction with the counter ion.

However, in the p-terphenyl - anthracone system with $[\text{anthracene}] = 3.59 \times 10^{-4}$ M the p-terphenyl cation decayed, with a half-life of
0.2 μsec, virtually to zero. The reaction of either cation with the
counter ion is much slower, so that, if any equilibrium is established,
it must be after the forward reaction has gone essentially to com-
pletion.

On the other hand, it might be argued that the plateau reached by
the decaying absorption at 685 nm in the biphenyl - μ-torphenyl and
biphenyl - pyrene systems represents the attainment of an equili-
brium. Even if this were true, it can be shown (Appendix E) that,
since [biphenyl] was kept constant, the method of analysis used would
still give the correct value for the forward reaction rate constant.

Furthermore, for an elementary reaction such as 26, it is true
that \( \frac{k_{26}}{k_{-26}} = K = \exp(-\Delta F^0/RT) \) where \( \Delta F^0 \) is the standard free-
energy increment of the reaction. If the solvation energy of the two
ions is nearly equal, then the difference in the gas phase ionization
potentials of the two aromatic compounds will give an approximate
value of \( \Delta F^0 \). (This assumes that \( \Delta S^0 \) and \( \Delta V^0 \) are approximately zero
for Reaction 26.) For the pairs μ-torphenyl - anthracene, biphenyl -
μ-torphenyl, and biphenyl - pyrene the ionization potential differ-
ences are -1.2, -0.17, and -1.1 eV respectively (51,52,53). This
gives approximately that \( \frac{k_{26}}{k_{-26}} \) equals 2 x 10^20, 8 x 10^2, and
6 x 10^23 respectively. The ratio of the pseudo-first-order rate con-
stants for the forward and reverse reactions are given by \( \frac{k_{26}[Ar_b]}{k_{-26}[Ar_a]} \). Since in these experiments \( [Ar_b]/[Ar_a] \) was in the range
2 x 10^-3 to 6 x 10^-2, it follows that the rate of the reverse reac-
tion was insignificant compared to that of the forward reaction in
all cases except possibly the biphenyl - μ-torphenyl system.
If the back reaction occurs in this latter system, then, as shown in Appendix B, the observed rate of decay of $D_b^+$ for biphényl$^+$ should increase with increasing [biphényl] at constant [p-terphényl]. With $[p$-terphényl] = $1.8 \times 10^{-4} M$, [biphényl] was varied from $10^{-2}$ to $2 \times 10^{-1} M$, but no increase in the decay rate was observed. Thus in this system also the back reaction is unimportant at the concentrations of biphényl and p-terphényl used in this study.

The bimolecular rate constants for the charge transfer reactions investigated above are listed in Table 1.

**TABLE 1**

RATE CONSTANTS FOR CHARGE TRANSFER REACTIONS

<table>
<thead>
<tr>
<th>$A_{r_a} - A_{r_b}$</th>
<th>$k \left( \text{M}^{-1} \text{sec}^{-1} \right)$</th>
<th>$T(\circ C)$</th>
<th>$\Delta F^0 \text{ (ev)}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-terphényl - Anthracene</td>
<td>$(0.1 \pm 0.0) \times 10^9$</td>
<td>24</td>
<td>$-1.2 \pm 0.3$</td>
</tr>
<tr>
<td>Biphényl - p-terphényl</td>
<td>$(5.1 \pm 1.0) \times 10^9$</td>
<td>25</td>
<td>$-0.17 \pm 0.1$</td>
</tr>
<tr>
<td>Biphényl - Pyrénè</td>
<td>$(9.9 \pm 1.0) \times 10^9$</td>
<td>24</td>
<td>$-1.4 \pm 0.2$</td>
</tr>
</tbody>
</table>

From references (51,52,53) assuming $\Delta F^0 = \Delta I.P.$

It is of interest to compare the rate constants for electron transfer measured above with rate constants for the reaction

$$A_{r_a}^- + A_{r_b} \rightarrow A_{r_a} + A_{r_b}^-$$

measured in isopropanol (5,7). Reaction 30 has been investigated for eleven different aromatic pairs; for two of these both the forward and reverse rate constants were measured. For seven of the pairs the rate constants were in the range $3.2 \times 10^9$ to $6.4 \times 10^9 \text{ M}^{-1} \text{sec}^{-1}$. 
with an average of $4.5 \times 10^9$ l mole$^{-1}$ sec$^{-1}$. This value agrees well with the calculated value for a diffusion controlled rate constant for reaction of molecules of these dimensions in isopropanol. The difference in the reduction potentials of the aromatic pair, $\Delta F^0$, is known in two cases and equals $-0.53$ and $-0.64$ ev respectively.

On the other hand, in six cases, including the two back reactions, where $\Delta F^0$ ranged from $-0.14$ to $+0.11$ ev the measured rate constants were significantly less than for a diffusion controlled reaction and showed a general decrease with increasing $\Delta F^0$.

These results were found (7) to be in reasonable quantitative agreement with calculations of a theory on electron transfer reactions put forth by Marcus (22-29). According to this theory

$$1/k_{obs} = 1/k_d + 1/k_{act}$$

where $k_{obs}$ is the observed rate constant and $k_d$ is the rate constant for a diffusion controlled reaction. $k_{act}$ is calculated by the theory. For constant temperature and solvent and for molecules of comparable dimensions, $k_d$ is a constant and $k_{act}$ is a function of $\Delta F^0$ only. It varies as $\exp[-\Delta F^0 - a(\Delta F^0)^2]/2RT$ where $a > 0$ depends on the solvent and molecular dimensions of the reactants.

If $k_d$ and $k_{act}$ are greatly different, then $k_{obs}$ will approximately equal the smaller of the two. Thus for large, positive $\Delta F^0$, $k_{obs} \approx k_{act}$ and will be vanishingly small. As $\Delta F^0$ decreases, $k_{act}$ and hence $k_{obs}$ will increase rapidly until a $\Delta F^0$ value is reached where $k_{act} = k_d$ and thus $k_{obs} = k_d/2$. As $\Delta F^0$ decreases still further, $k_{obs}$ will level off and rise slowly to $k_d$ in the limit. Figure 28 shows the log of measured rate constants (7) for Reaction 30 plotted versus
Figure 28: Bimolecular rate constants for electron transfer reactions plotted versus $\Delta F^0$. $\circ$, electron transfer from an aromatic anion to a neutral aromatic molecule (from [7] with permission of the author); $\triangle$, electron transfer from a neutral aromatic molecule to an aromatic cation.
$\Delta F^\circ$. The predicted behavior is observed. For $\Delta F^\circ$ less than about 
-0.14 eV the rate constants are at the diffusion-controlled limit.

The theory of Marcus is equally applicable to the electron transfer reactions investigated in this study. The fact that here electrons are transferred from a neutral to a positively charged species instead of from a negatively charged to a neutral species is not important. $\Delta F^\circ$ is now given approximately by the difference in the gas phase ionization potentials of the two arcatic compounds, if the solvation energies of the two ions are assumed to be comparable and $\Delta \Omega^\circ \approx 0 \approx \Delta F^\circ$.

The only other difference between this and the arcatic anion study is the solvent. For given temperature and molecular dimensions of reactants, $k_d$ will depend only on the viscosity of the solvent (Appendix B). Since 1,2-DCB is less viscous than isopropanol, $k_d$ will be higher in the present case. $k_{act}$ depends on the solvent primarily because it is a function of $(1/D_{op} - 1/D_g)$ where $D_{op}$ and $D_g$ are the optical and static dielectric constants of the solvent, respectively. $(1/D_{op} - 1/D_g)$ is equal to 0.582 and 0.575 for isopropanol and 1,2-DCB respectively (5h). Thus for a given $\Delta F^\circ$, $k_{act}$ will be essentially the same in both solvents. Thus in 1,2-DCB, $k_{obs}$ should show the same increase as in isopropanol with decreasing $\Delta F^\circ$, but should rise to a higher limiting value of $k_d$.

Table 1 lists the values of $\Delta F^\circ$ for the pairs investigated here. Figure 20 shows the constants measured in this work plotted on the same scale as those from Reference 7. Clearly the two highest rate
constants (where $\Delta F^0 = -1.4$ and $-1.2$ ev) are essentially diffusion-controlled and are larger than $k_d$ in isopropanol by about a factor of two. For the biphenyl - terphenyl pair the rate constant is somewhat smaller and it appears that $\Delta F^0$ for this pair is such that $k_{act}$ may be significant compared to $k_d$ in determining $k_{obs}$. 
APPENDIX A

INTEGRATION OF RATE EQUATIONS FOR FORMATION OF THE AROMATIC CATION

Suppose

\[ S \xrightarrow{\text{radiation}} S^+ + e^- \quad (13) \]
\[ S^+ + \text{Ar} \rightarrow S + \text{Ar}^+ \quad (10) \]
\[ S^+ \rightarrow \text{products} \quad (14) \]

so that

\[ \frac{d[\text{Ar}^+]}{dt} = k_{10}[\text{Ar}][S^+] \quad , \quad 0 \leq t < \infty \quad (I) \]
\[ \frac{d[S^+]}{dt} = k_{13} - (k_{10}[\text{Ar}] + k_{14})[S^+] \quad , \quad 0 \leq t \leq p \quad (II) \]
\[ = -(k_{10}[\text{Ar}] + k_{14})[S^+] \quad , \quad p < t < \infty \quad (III) \]

and that at \( t = 0 \)

\[ [S^+]_0 = [\text{Ar}^+]_0 = 0 \quad (IV) \]

Rearrangement of Equation II and integration from \( t = 0 \) to \( t \leq p \) gives

\[ \int_0^t \frac{d[S^+]}{k_{13} - \kappa[S^+]} = \int_0^t dt \quad (V) \]

where \( \kappa = (k_{10}[\text{Ar}] + k_{14}) \), which is essentially constant if Reactions 10 and 14 are pseudo-first-order.

\[ -\{\ln(k_{13} - \kappa[S^+]) - \ln k_{13}\}/\kappa = t \quad (VI) \]
\[ 1 - \kappa[S^+]/k_{13} = \exp(-\kappa t) \quad (VII) \]
\[ [S^+] = k_{13}\{1 - \exp(-\kappa t)\}/\kappa \quad , \quad 0 \leq t \leq p \quad (VIII) \]
Substituting Equation VIII into Equation I and again integrating from \( t = 0 \) to \( t \leq p \) gives

\[
\int_{0}^{[Ar^+]^i} d[Ar^+]^i = \int_{0}^{t} \left\{ k_{10} [Ar] k_{13}/\kappa \right\} \left\{ 1 - \exp(-\kappa t) \right\} dt^i \quad \text{(IX)}
\]

\[
[Ar^+]^i = \frac{k_{10} k_{13} [Ar]}{\kappa} \left\{ t + \exp(-\kappa t) - 1 \right\}, \quad 0 \leq t \leq p \quad \text{(X)}
\]

At the end of the pulse, \( t = p \), Equations VIII and X become

\[
[S^+]_p = k_{13} \left\{ 1 - \exp(-\kappa p) \right\}/\kappa \quad \text{(XI)}
\]

\[
[Ar^+]_p = \frac{k_{10} k_{13} [Ar]}{\kappa} \left\{ p - (1 - \exp(-\kappa p)) \right\} \quad \text{(XII)}
\]

Integration of Equation III after the pulse gives

\[
\int_{[S^+]}_{p} \frac{d[S^+]}{[S^+]^i} = -\int_{p}^{t} \kappa dt^i \quad \text{(XIII)}
\]

\[
\ln \left\{ [S^+] / [S^+], p \right\} = -\kappa(t - p) \quad \text{(XIV)}
\]

\[
[S^+] = [S^+], p \exp(-\kappa(t - p)), \quad t \geq p \quad \text{(XV)}
\]

Substitution of Equation XV into Equation I and integrating from \( t \geq p \) to \( \infty \) gives

\[
\int_{[Ar^+]}_{\infty} d[Ar^+]^i = \int_{t}^{\infty} k_{10} [Ar] [S^+], p \exp(\kappa p) \exp(-\kappa t) dt^i \quad \text{(XVI)}
\]

\[
[Ar^+]_{\infty} = [Ar^+] = \left\{ k_{10} [Ar] [S^+], p \exp(\kappa p)/\kappa \right\} \exp(-\kappa t), t \geq p \quad \text{(XVII)}
\]

Define \( r = (\ln 2)/\kappa \). Then at time \( t_1 + r \), \( t_1 \geq p \), Equation XVII gives

\[
[Ar^+]_{\infty} = [Ar^+]_{t_1 + r} = \left\{ k_{10} [Ar] [S^+], p \exp(\kappa p)/\kappa \right\} \exp\left\{ -\kappa(t_1 + (\ln 2)/\kappa) \right\} \quad \text{(XVIII)}
\]

\[
[Ar^+]_{\infty} = [Ar^+]_{t_1 + r} = \left\{ k_{10} [Ar] [S^+], p \exp(\kappa p)/\kappa \right\} (1/2) \exp(-\kappa t_1) \quad \text{(XIX)}
\]
Thus

$$[\text{Ar}^+]_\infty - [\text{Ar}^+]_{t_1} = ([\text{Ar}^+]_\infty - [\text{Ar}^+]_{t_2})(1/2), \quad t_1 \geq p \quad (XX)$$

Thus one half of the total growth in $[\text{Ar}^+]$, after an arbitrary time $\geq p$, will be accomplished in the time $t$, which may be called the half-time for the growth of $[\text{Ar}^+]$ after the pulse.

Letting $t = p$ in Equation XVII gives

$$[\text{Ar}^+]_\infty - [\text{Ar}^+]_p = \frac{k_{10}[\text{Ar}][S^+]}{\kappa} \quad (XXI)$$

Substitution of Equation XI into XXI gives

$$[\text{Ar}^+]_\infty - [\text{Ar}^+]_p = \frac{k_{13}k_{10}[\text{Ar}][1 - \exp(-\kappa p)]}{\kappa^2} \quad (XXII)$$

Substitution of Equation XII into XXII gives

$$[\text{Ar}^+]_\infty = \frac{pk_{13}k_{10}[\text{Ar}]}{\kappa} \quad (XXIII)$$

From Equations XXII and XXIII it follows that the percentage, $Q$, of the total yield of $\text{Ar}^+$ produced after the pulse is given by

$$Q = 100\left(\frac{[\text{Ar}^+]_\infty - [\text{Ar}^+]_p}{[\text{Ar}^+]_\infty}\right) = \frac{100}{\kappa p} \left(1 - \exp(-\kappa p)\right) \quad (XXIV)$$
APPENDIX B

CALCULATION OF DIFFUSION-CONTROLLED RATE CONSTANTS

If molecules a and b react and the rate of their reaction is determined by the rate at which they diffuse together, then the rate constant can be calculated using the formula of Bäckström and Sandros (55,56)

\[ k_d = \frac{2RT}{(3 \times 10^3)\eta} \left( 2 + \frac{r_a}{r_b} + \frac{r_b}{r_a} \right) \]  

where \( r_i \) is the radius of the \( i \)th molecule, treated as a sphere, and \( \eta \) is the viscosity of the solvent.

The variation of the viscosity of a liquid such as 1,2-DCS with temperature over a small range is expressed reasonably well by (57)

\[ \eta = A \exp(\varepsilon/RT) \]  

where \( A \) and \( \varepsilon \) are constants. Thus a plot of \( \log \eta \) versus \( 1/T \) should be linear. Figure 29 shows that this is true over a considerable range and gives \( \eta \) at any desired temperature about that range.

The ratio \( r_a/r_b \) is more difficult to determine since the molecules of interest here are not spherical. One way to compute a sort of "average" radius for a molecule is to calculate its approximate volume and then calculate the radius of a sphere of equal volume. Thus

\[ \frac{r_a}{r_b} = \frac{3}{\sqrt[3]{V_a/V_b}} \]  

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Figure 29: Plot of $\log \eta$ versus $1/T \times 10^3$. The data are from Reference 58. The line through the data points gives the viscosity at any temperature in this range, (a) $+25^\circ C$; (b) $-31^\circ C$. 
where $V_a$ and $V_b$ are the approximate volumes of the two molecules. Figure 30 shows diagrams of the biphenyl, $p$-torphenyl, and 1,2-dichloroethane molecules, respectively, with the bond lengths given in Angstroms ($59,60$). Because of internal rotation these molecules may be considered to be approximately cylindrical. This gives 15.5, 135, and 197 Å$^3$ for the volumes of 1,2-DCE, biphenyl, and $p$-torphenyl respectively. If the volume of 1,2-DCE$^+$ is taken to be nearly equal to that of the neutral molecule, substitution into Equation III gives:

$$\frac{r(\text{biphenyl})}{r(\text{1,2-DCE}^+)} = 2.1$$

$$\frac{r(\text{$p$-torphenyl})}{r(\text{1,2-DCE}^+)} = 2.3$$

Although these ratios are only approximate, they are probably more accurate than the calculation of either individual radius. Furthermore, in Equation I the ratio is added to its inverse. If the ratio is too large, its inverse will be too small, and vice versa. Thus the value of $k_d$ will not be much affected by even rather large errors in the calculation of the molecular radii.

Substitution of the appropriate values into Equation I gives $k_d = 9.8 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ for biphenyl + 1,2-DCE$^+$ at 25°C and $k_d = 3.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ for $p$-torphenyl + 1,2-DCE$^+$ at -31°C.

The largest source of error in applying Equation I is the uncertain value of the ratio $r_a/r_b$. However the equation itself is only an approximation since the theory leading to its derivation is not exact. Nevertheless one might expect Equation I to be somewhat more accurate in showing relative changes in $k_d$ over small ranges of temperature and molecular size.
Figure 30: Approximate molecular dimensions (in Angstroms) of the molecules biphenyl, para-terphenyl, and 1,2-dichloroethane. Bond lengths are from References 59 and 60.


APPENDIX C

INTEGRATION OF RATE EQUATIONS FOR
THE DECAY OF AN ABSORBER

FIRST-ORDER DECAY

Suppose that a reactant, \( a \), decays with a first-order or pseudo-first-order rate law. Then

\[
\frac{-d[a]}{dt} = k'[a]
\]

where \( k' \) is the first-order (or pseudo-first-order) rate constant.

Letting \( [a]_p \) be the concentration of \( a \) at the end of the pulse, and defining the zero of time as the end of the pulse, one has by integration

\[
\int_{[a]}^{[a]_p} \frac{d[a]}{[a]} = -k' \int_0^t dt
\]

\[
\ln[a] = \ln[a]_p - k't
\]

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

\[
\ln D - \ln(\epsilon_a d) = \ln D_p - \ln(\epsilon_a d) - k't
\]

or simply

\[
\ln D = \ln D_p - k't
\]

A plot of \( \ln D \) versus \( t \) will be linear and

\[
k' = -\sigma
\]

where \( \sigma \) is the slope of the graph.
SECOND-ORDER DECAY

Suppose that a decays by reaction with itself or by reaction with b, where \([b]_p = [a]_p\). (The stoichiometry of the latter reaction is assumed to be one to one.) Then

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

where \(k_s\) is the second-order rate constant for the reaction. Again integrating from the end of the pulse

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

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

\[
\frac{1}{[a]} = k_s t + \frac{1}{[a]_p}\]  \hspace{1cm} (X)

Substituting \(D/\epsilon_{ad}\) for \([a]\) gives

\[
\frac{\epsilon_{ad}}{D} = k_s t + \frac{\epsilon_{ad}}{D_p}\]  \hspace{1cm} (XI)

\[
\frac{1}{D} = \frac{k_s t}{\epsilon_{ad}} + \frac{1}{D_p}\]  \hspace{1cm} (XII)

Thus a plot of \(1/D\) versus \(t\) will be linear and

\[
k_s/\epsilon_{ad} = \sigma, \text{ the slope of the graph.}\]  \hspace{1cm} (XIII)

MIXED FIRST- AND SECOND-ORDER DECAY

Suppose the decay of a can be represented by

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

Let \(\theta\) be a positive constant; then

\[
\int_{[a]_t}^{[a]_t + \theta} \frac{d[a]}{(k_f[a] + k_s[a]^2)} = -\int_{t}^{t+\theta} dt\]  \hspace{1cm} (XV)
Substitution of $D/d$ for $[a]$ gives

$$\frac{1}{D_t + \theta} = \frac{\exp(k_f \theta)}{D_t} + \frac{k_s \{\exp(k_f \theta) - 1\}}{k_f}$$

Thus a plot of $1/D_t + \theta$ versus $1/D_t$ will be linear. $\theta$ is conveniently chosen to be about 5 to 10 per cent of the total time over which the decay is observed. Optical densities are measured at pairs of time points, $t$ and $t + \theta$, at various places along the curve. If $\sigma$ is the slope and $\iota$ the vertical-axis intercept of the graph, then it follows from Equation XX that

$$k_f = \frac{(\ln \sigma)/\theta}{(XX)}$$

and

$$k_s/j_a d = \frac{\iota \ln \sigma}{\theta(\sigma - 1)}$$

(XXI)
DATA ANALYSIS WHEN TWO SPECIES ABSORB

Suppose that chemical species $a$ and $b$ are present in a solution and that these are the only species which absorb at wavelengths $\lambda_1$ and $\lambda_2$. Suppose further that species $a$ is decaying, so that, after a certain time $t = q$, only $b$ is present. Then since $D_t^a = \epsilon_b^a[b]_t d$ it follows that

$$\log D_t^1 - \log D_t^2 = \log(\epsilon_b^1/\epsilon_b^2), \quad t \geq q \quad (I)$$

where superscripts 1 and 2 denote wavelengths $\lambda_1$ and $\lambda_2$ respectively. Thus one can measure $\log(\epsilon_b^1/\epsilon_b^2)$ by measuring $D_t^1$ and $D_t^2$ at some arbitrary point in time, $t \geq q$.

However, if the optical densities are small and the oscilloscope traces are noisy, the value one obtains will depend somewhat on the time point chosen. A more accurate technique is to make plots of $\log D_t^1$ and $\log D_t^2$ versus $t$, where $t \geq q$, and the same zero of time is used in each plot. Then the two graphs will be separated vertically by the constant amount, $\log(\epsilon_b^1/\epsilon_b^2)$. If the two plots are made on separate sheets of transparent paper, the one can be moved vertically over the other until the best superposition of the two graphs is achieved. The amount of displacement required gives $\log(\epsilon_b^1/\epsilon_b^2)$.

At any time it will be true that
\[ D_t^1 = \epsilon_a^1 [a]_t^d + \epsilon_b^1 [b]_t^d \]  
and
\[ D_t^2 = \epsilon_a^2 [a]_t^d + \epsilon_b^2 [b]_t^d \]

Multiplication of Equation III by the value of \( \epsilon_b^1 / \epsilon_b^2 \) obtained above gives
\[ \left( \epsilon_b^1 / \epsilon_b^2 \right) D_t^2 = \left( \epsilon_b^1 / \epsilon_b^2 \right) \epsilon_a^2 [a]_t^d + \epsilon_b^2 [b]_t^d \]  

Subtraction of Equation IV from II gives
\[ D_t^1 - \left( \epsilon_b^1 / \epsilon_b^2 \right) D_t^2 = \left\{ \epsilon_a^1 - \left( \epsilon_b^1 / \epsilon_b^2 \right) \epsilon_a^2 \right\} [a]_t^d \]  
or
\[ D_t^1 = \epsilon^' [a]_t = D_t^1 - \left( \epsilon_b^1 / \epsilon_b^2 \right) D_t^2 \]  

where \( D_t^1 \) is defined by this equation and \( \epsilon^' \) is a constant equal to
\[ \left\{ \epsilon_a^1 - \left( \epsilon_b^1 / \epsilon_b^2 \right) \epsilon_a^2 \right\} [a]_t^d \]. The right hand member of Equation VI is measurable and gives \( D_t^1 \), which is proportional to \([a]_t^d \).

In a pulse radiolysis experiment the wavelengths \( \lambda_1 \) and \( \lambda_2 \) can be observed simultaneously, and the zero of time may be chosen arbitrarily, but would usually be taken as the end of the pulse. Alternatively, if the pulse is reproducible, the wavelengths \( \lambda_1 \) and \( \lambda_2 \) may be observed during subsequent pulses 1 and 2 respectively. This method gives a better quality of signal at each of the two wavelengths. In this case the zero of time is taken as the end of the pulse in each picture. If the dose is identical from pulses 1 and 2, then the above derivation is applicable and exact.

On the other hand, if there are small differences in dose between the two pulses, then \([a]_t^d\) and \([b]_t^d\) at a given time will depend on the pulse, since the zero of time is always taken as the end of the pulse. However, if the difference in dose is only a few per cent, then to a
good approximation \([a]_t^2 = \gamma[a]_t^1\) and \([b]_t^2 = \delta[b]_t^1\), where \(\gamma\) and \(\delta\) are constants close to unity and the superscripts designate the number of the pulse. (Actually this approximation is exact for species undergoing pseudo-first-order reactions, such as the cation in the charge transfer reaction.)

Now superposition of plots of \(\log D_t^1\) and \(\log D_t^2\) versus \(t\), \(t \geq q\), gives \((e^1_\gamma/e^2_\gamma)\), (see Equation I). Equation IV is now

\[
\frac{e^1_\gamma}{e^2_\gamma}D_t^2 = \left(\frac{e^1_\gamma}{e^2_\gamma}\right)e^2_\gamma[a]_t^1 + e^1_\gamma[b]_t^1
\]

Subtraction from Equation II gives

\[
D_t^1 - (e^1_\gamma/e^2_\gamma)D_t^2 = \left\{e^1_\gamma - (e^1_\gamma/e^2_\gamma)e^2_\gamma\right\}[a]_t^1
\]

or

\[
D_t'' = e''[a]_t^1 = D_t^1 - (e^1_\gamma/e^2_\gamma)D_t^2
\]

The right hand member of this equation is measurable and gives \(D_t''\), which is proportional to \([a]_t\) following pulse 1.

Thus, since the value of the proportionality constant \((\epsilon'\) or \(\epsilon''\)) is unimportant in pseudo-first-order kinetics, it does not matter in this case if the dose differs slightly between the two pictures.

Furthermore, one does not need to know the constants \(\gamma\) and \(\delta\).
APPENDIX E

DATA ANALYSIS WHEN TWO SPECIES ABSORB AND ESTABLISH AN EQUILIBRIUM BETWEEN THEMSELVES

Suppose that both the forward and reverse electron transfer reactions are important

\[ \text{Ar}_a^+ + \text{Ar}_b \rightarrow \text{Ar}_a + \text{Ar}_b^+ \quad (1) \]

and that, at the concentrations of \( \text{Ar}_a \) and \( \text{Ar}_b \) used, an equilibrium is established quickly relative to the decay time of the two cations, caused by reaction with the counter ion. Let \( t = q \) be a time after which the equilibrium is essentially established. Then

\[ k_1[\text{Ar}_b][\text{Ar}_a^+] = k_1[\text{Ar}_a][\text{Ar}_b^+], \quad t \geq q \quad (I) \]

To simplify notation let \( a = \text{Ar}_a^+ \) and \( b = \text{Ar}_b^+ \) and define \( K' = k_1[\text{Ar}_b]/k_1[\text{Ar}_a] \) \( (K' \) is a pseudo-equilibrium constant). In this notation Equation I rearranges to give

\[ [b]_t = K'[a]_t, \quad t \geq q \quad (II) \]

It follows that, for \( t \geq q \)

\[ D_t^2 = \epsilon_a^2[a]_t d + \epsilon_b^2[b]_t d = \left\{ \epsilon_a^2 + K'\epsilon_b^2 \right\}[a]_t d, \quad t \geq q \quad (III) \]

Thus, for observations at wavelengths \( \lambda_1 \) and \( \lambda_2 \)

\[ \log D_t^1 - \log D_t^2 = \log \left[ \left\{ \frac{\epsilon_a^1 + K'\epsilon_b^1}{\epsilon_a^2 + K'\epsilon_b^2} \right\} \right], \quad t \geq q \quad (IV) \]

where \( D_t^1 \) and \( D_t^2 \) are defined by Equation IV. If one plots \( \log D_t^1 \) and
log $D_t^1$ versus $t$ and displaces the graphs vertically until they coincide for $t \geq q$, the amount of displacement will give a measure of $E^1/E^2$, which is a constant.

This value of $E^1/E^2$ can then be used to obtain $D_t^1 = (E^1/E^2)D_t^2$ at any time, in particular, when $0 \leq t \leq q$. By Equation III

$$D_t^1 - (E^1/E^2)D_t^2 = \left\{ \epsilon_a^1 - (E^1/E^2) \epsilon_a^2 \right\} [a]_t d + \left\{ \epsilon_b^1 - (E^1/E^2) \epsilon_b^2 \right\} [b]_t d$$

$$= \left\{ E^2 \epsilon_a^1 - E^1 \epsilon_a^2 \right\} [a]_t d/E^2 + \left\{ E^2 \epsilon_b^1 - E^1 \epsilon_b^2 \right\} [b]_t d/E^2$$

But

$$E^2 \epsilon_a^1 - E^1 \epsilon_a^2 = (\epsilon_a^1 - \epsilon_a^2) K^1$$

and

$$E^2 \epsilon_b^1 - E^1 \epsilon_b^2 = -(\epsilon_a^1 - \epsilon_a^2)$$

Substitution of Equations VII and VIII into VI gives

$$D_t^1 - (E^1/E^2)D_t^2 = \left\{ \frac{1}{a} \epsilon_a^1 \epsilon_a^2 \right\} d \left\{ K^1 [a]_t - [b]_t \right\} = D_t^1$$

The left hand member of this equation is measurable and gives a quantity, $D_t^1$, which is proportional to $[k^1[a]_t - [b]_t]$. The differential equations giving the rate of change of $[a]_t$ and $[b]_t$ are

$$-d[a]_t/dt = k_1[Ar_b][a]_t - k_{-1}[Ar_a][b]_t + k_{at}[a]_t \quad (X)$$

$$+d[b]_t/dt = k_1[Ar_b][a]_t - k_{-1}[Ar_a][b]_t - k_{bt}[b]_t \quad (XI)$$

where the last term in each equation represents the decay of the aromatic cation by reaction with the counter ion. $k_{at}$ and $k_{bt}$ are relatively slowly decreasing functions of time. Multiplying Equation X by $K^1$ gives
\[ \frac{d(k'[a]^t)}{dt} = k_1[Ar_b]K'[a]^t - k_1[Ar_b][b]^t + k_{at}K'[a]^t \]  
also Equation XI can be written

\[ + \frac{d[b]^t}{dt} = k_{-1}[Ar_a]K'[a]^t - k_{-1}[Ar_a][b]^t - k_{bt}[b]^t \]

Addition of Equations XII and XIII gives

\[ - \frac{d(b^t)}{dt} = \left\{ k_1[Ar_b] + k_{-1}[Ar_a] \right\} \left\{ K'[a]^t - [b]^t \right\} + k_{at}K'[a]^t - k_{bt}[b]^t \]  

If the assumption is made that both aromatic cations react with the counter ion at about the same rate, Equation XIV becomes

\[ - \frac{d(b^t)}{dt} = \left\{ k_1[Ar_b] + k_{-1}[Ar_a] \right\} \left\{ K'[a]^t - [b]^t \right\} + k_{t}\left\{ K'[a]^t - [b]^t \right\} \]  

The accuracy of the approximation that \( k_{at} = k_{bt} \) is not very critical if both are small compared to \( k_1[Ar_b] + k_{-1}[Ar_a] \), i.e., if the decay rate of the aromatic cations by reaction with the counter ion is slow compared to the rate at which equilibrium is reached. Furthermore, if this is true, the same approximation can be made that was made in the case of no back reaction, namely, that \( k_t \approx k_p \) over the time range of interest, i.e., \( t < q \). Thus Equation XV becomes simply

\[ - \frac{d(b^t)}{dt} \approx \left\{ k_1[Ar_b] + k_{-1}[Ar_a] + k_p \right\} \left\{ K'[a]^t - [b]^t \right\} \]

Thus the variable \( K'[a]^t - [b]^t \) decays by a first-order rate law. \( D_t^t \), measured above, is proportional to this variable, so that a plot of log \( D_t^t \) versus \( t \) will be linear with a slope \( \sigma = k_1[Ar_b] + k_{-1}[Ar_a] + k_p \). If \([Ar_a]\) is constant, as it was in the experiments of this study, then a plot of \( \sigma \) versus \([Ar_b]\) will be linear with a slope equal to \( k_1 \), the bimolecular rate constant for the forward charge transfer reaction.
Thus the method of data analysis used for the pairs biphenyl - p-terphenyl and biphenyl - pyrene will give the correct value of the forward charge transfer rate constant whether or not the back reaction is occurring. No assumption needs to be made about the occurrence or rate of the back reaction.

On the other hand, if the back reaction does occur with a significant rate at the value of \([\text{Ar}_a]\) used, then the slope, \(\sigma\), measured above should increase linearly with \([\text{Ar}_a]\) if \([\text{Ar}_b]\) is kept constant. If the back reaction does not occur, no such increase will be observed. This provides a test for the occurrence of the back reaction (i.e., with a rate which is significant compared to that of the forward reaction) and, if it occurs, gives the rate constant from a plot of \(\sigma\) versus \([\text{Ar}_a]\).

False evidence for a back reaction may be observed if there is an impurity in \(\text{Ar}_a\) that causes significant decay of \(\text{Ar}_a^+\). This will cause \(\text{Ar}_a^+\) to decay faster as \([\text{Ar}_a]\) is increased and may give the appearance of a back reaction. One can check this possibility by measuring the effect of \([\text{Ar}_a]\) on the decay rate of \(\text{Ar}_a^+\) in the absence of \(\text{Ar}_b\). In such a system there is obviously no back charge transfer reaction.
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