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FAST KINETIC STUDIES OF ORGANIC CATIONS IN SOLUTION

DISSERTATION

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

By
Richard Joseph Sujdak, B.S., M.S.

* * * * *

The Ohio State University
1977

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ACKNOWLEDGMENT

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INTRODUCTION

Many important organic chemical reactions proceed by ionic mechanisms in liquid solutions. Of the various types of organic intermediates, carbonium ions are among the most important and the most extensively studied. The radiation chemical technique of pulse radiolysis\(^1\) has proven to be useful in the determination of the optical absorption spectra and the absolute reactivities of molecular ions,\(^2\) including carbonium ions.\(^3\) Investigating the formation processes of carbonium ions in pulse irradiated solutions provides information about the rate and mechanism of positive charge migration in irradiated solutions.

Irradiation of dilute solutions with high energy electrons results in ionization of the solvent. The primary ionization process is:

\[
e^- + S = S^+ + 2e^- \quad (1)
\]

Direct ionization of the solute by high energy electrons is negligible at the doses used for the experiments reported in this dissertation, since the concentration of the solvent greatly exceeds the concentration of the solute.

The products of Reaction (1) are the electron, a reducing species, and the cation radical of the solvent, an oxidizing species.
Under appropriate circumstances, these transients may react with the solute to produce radical ions. For example, in cyclohexane both the positive radicals and the negative radicals of aromatic compounds are generated\(^4\) according to the following reactions:

\[
S^+ + Ar = Ar^+ + S
\]  \hspace{1cm} (2)

and

\[
e^- + Ar = Ar^-
\]  \hspace{1cm} (3)

However, by selecting the proper chemical systems, only one of the solute ions will be produced.

To eliminate cations derived from the solute, three possibilities exist. First, the solvent could be chosen such that the ionization potential of the solvent is less than the ionization potential of the solute (ignoring solvation effects). Second, the solvent cation could be scavenged by a second additive, to the exclusion of Reaction (2). Finally, solvents can be chosen such that the initial ion reacts with the solvent to produce an ion that does not exchange charge with the solute. For example, in aliphatic alcohols ROH\(^+\) abstracts a proton from the solvent, ROH. The product, ROH\(_2^+\), does not ionize most aromatic solutes.\(^5\) Extensive studies have been made of the reactions of aromatic anions in alcohol solvents.\(^3,5,6\)

The formation of anions derived from the solute can be eliminated by analogous methods. The electron could be scavenged to the exclusion of Reaction (3) by the addition of molecular oxygen or nitrous oxide. There is substantial evidence that halocarbons
react with electrons in a dissociative attachment reaction to form halide ion.

\[ \text{e}^- + RX = R^+ + X^- \]  

(4)

In the gas phase Reaction (4) is very efficient whenever the electron affinity of X exceeds the bond dissociation energy of RX. Furthermore, the removal of solvated electrons from solutions to which RX has been added has been shown, whenever the spectrum of R+ is known, to be accompanied by the concurrent formation of R+. Finally, the scavenging effect of RX on the electron is indicated by the suppression of yields of solute anions by addition of RX and by the observation that radical anions and carbonanions have never been observed in 1,2-dichloroethane. Thus, the electron, a transient that could be very reactive toward the solute, is localized on a relatively unreactive chloride ion.

Halocarbons could either be added to a solution as a scavenger of the electron or be used as the solvent itself to study solute cations in the absence of solute anions. Although it is not imperative that halocarbon solvents be used in irradiation studies of organic cations, they are well suited for this purpose.

The formation of aromatic cation radicals in solids and the formation and reactivity of these ions in liquids has been the subject of a substantial volume of work. The first step of the radiolysis is the ionization of the solvent, Reaction (1). Since the solute is not ionized as a direct result of the radiation in dilute solutions, the positive charge center in the solution must
migrate the distance of many solvent molecules toward the solute. However, in solid solutions molecular diffusion is severely limited. These facts have led to the suggestion that a resonance charge transfer process occurs that is responsible for the migration of the positive charge.17

\[ RX^+ + RX = RX + RX^+ \]  

Therefore, the rate of formation of the solute cations by Reaction (2) may likely occur at a rate that is not limited by diffusion.

Investigations of the mechanism of the formation of solute cations in liquids have been rather limited. However, it has been suggested that the rate of formation of several aromatic cation radicals in 1,2-dichloroethane (DCE) do occur at a rate greater than diffusion.16 More recent work on n-butyl chloride solutions of biphenyl at 133 K seem to indicate that most of the biphenyl cations are formed by a rapid process during irradiation and a smaller portion is formed by a diffusive process following irradiation.14 The investigations reported in this dissertation have included the formation of the biphenyl cation and the terphenyl cation in DCE at room temperature. The mechanism of formation is discussed in terms of the new data and compared to the previous suggestions.

As indicated by Reaction (3), non-dissociative electron attachment yields the radical anion of the solute. Dissociative
electron attachment to symmetrical organometallic compounds results in formation of carbanion. For example, in tetrahydrofuran

$$e^{-}_{sol} + (\text{PhCH}_2)_2\text{Hg} = \text{PhCH}_2^- + \text{PhCH}_2\text{Hg}^.$$  \hspace{1cm} (6)

Similarly, if appropriate solutes are selected to undergo dissociative ionization by electron transfer to the solvent cation, carbonium ions will be formed according to the reaction

$$S^+ + PX = S + P^+ + X.$$  \hspace{1cm} (7)

The carbonium ion, $P^+$, is an organic cation that may be represented as a structure containing a positively charged trivalent carbon atom. Carbonium ions, or carbocations, have been directly observed both as stable species in equilibrium systems and as transients in reacting systems. The reactions of carbonium ions are those of an electrophile. Classes of reactions in which these cations are believed to be intermediates include unimolecular solvolyses, polymerizations, Friedel-Crafts reactions, eliminations yielding olefins, and reaction involving intramolecular or intermolecular hydride and alkyl shifts.

Because many carbonium ions are often highly reactive intermediates, their reactions are too rapid for direct kinetic study by methods limited to millisecond time resolution. Consequently, much of the current knowledge concerning their chemical reactivity has resulted from competition experiments, which indicate only
relative reactivity. Determination of absolute rates for fast reaction had been limited to the application of stopped flow methods with their millisecond time resolution.\textsuperscript{20}

Application of the fast reaction method of pulse radiolysis to the investigation of carbocations makes it possible to form highly reactive ions on a submicrosecond time scale and to determine their optical absorption spectra. Because of the time resolution this method affords, absolute rate constants for many of their elementary reactions can be determined, from which the magnitude of steric and electronic effects can be evaluated.

The positive identification of a carbonium ion as a transient generated in pulse irradiated systems was first made by Capellos and Allen.\textsuperscript{21,22} In the course of their studies on cation yields, they succeeded in forming the trityl cation, $\text{Ph}_3\text{C}^+$, in a number of solvents. In an extension of their work on the reactivity of aromatic cation radicals,\textsuperscript{2} Jones and Dorfman produced the trityl, $\text{Ph}_3\text{C}^+$, the benzhydryl, $\text{Ph}_2\text{CH}^+$, and the benzyl, $\text{PhCH}_2^+$, cations in pulse irradiated solutions of 1,2-dichloroethane (1,2-DCE) and selected precursor compounds.\textsuperscript{12} The trityl and benzhydryl cations were identified by comparison with their reported optical absorption spectra. Since the solvent was a halocarbon, it was expected that the corresponding carbanions would not be formed. Scavenger studies confirmed that similar organic anions were not present in these solutions.

Since the optical absorption spectrum of the benzyl cation had not been previously reported, its identification proceeded somewhat differently. Upon irradiation of solutions of dibenzylmercury in
1,2-DCE, a transient with its absorption maximum at 363 nm is formed. That the species is cationic is clearly established by the effects of selective scavengers. Assignment of this 363 nm band to the benzyl cation is based upon the observation that the occurrence of this band is common to a variety of sufficiently different precursor compounds.

The work presented in this dissertation extends the investigation of these three ary carbonium ions to the study of their reactivity with a variety of nucleophiles. In order to distinguish between hydride abstraction and formation of a protonated ether, deuterium isotope experiments were conducted for the reaction of the benzhydryl cation with methanol. The rates and mechanism for the formation of carbonium ions were also investigated. The results help to identify the nature of positive charge migration in DCE in the liquid phase.
EXPERIMENTAL

The general method of pulse radiolysis has been concisely described elsewhere.\(^1\) The following descriptions present details of the specific procedures and equipment involved in this investigation.

**Pulse Irradiation**

The source of high energy electrons was a Varian linear accelerator, Model V-7715-A. The accelerator could be operated in either the steady state mode or the stored energy mode. In steady state operation, the electron pulse is long compared to the time necessary to propagate the microwave field along the beam axis. Under this condition, the rate of energy extraction by the electrons equals the rate of energy input from the magnetron. Thus, a steady state is reached. The pulse duration in this mode could be varied from 0.1 to 1.4 \(\mu\)secs. For the experiments reported herein, the pulse varied from 0.2 to 0.8 \(\mu\)secs. The mean electron energy was about 3.5 MeV with 70\% of the electrons being within \(\pm 0.6\) MeV of this value.\(^2\) Beam currents were approximately 350 milliamps in this mode.

In the stored energy mode, the duration of the electron pulse is comparable with the time necessary to propagate the microwave along the beam axis. The electrons then extract energy from the microwave field that is already existent in the waveguide. The result
is that the electrons are accelerated to higher energies in the stored mode than in the steady state mode. However, a consequence of extracting the stored energy is a broader energy spectrum of the electrons. This phenomenon is explained by the following considerations. The energy available to accelerate an electron at a particular point along the waveguide is \( E_0 \) at time \( t_0 \). At time \( t_0 + t \), another electron will pass the same portion of the waveguide. However, the energy available to accelerate the second electron will be less than \( E_0 \), since the first electron extracted a portion of \( E_0 \). In the stored energy mode the mean electron energy varies from 5 MeV at 10 nsecs after the start of the pulse to 4 MeV at 50 nsecs after the start of the pulse. At any particular time, 70% of the electrons are within a range of \( \pm 0.6 \) MeV, as in the steady state mode. Therefore, approximately 90% of the electrons have energies between 3.4 MeV and 5.6 MeV for a 50 nsec pulse. The maximum beam currents in the stored mode were approximately 600 milliamps. Shorter pulse lengths of the electron beam injected into the waveguide during stored energy operation enable the attainment of higher beam currents at the irradiation cell. The higher intensity of the electron beam in the stored mode allowed measurable quantities of transients to be formed in shorter times than the steady state mode permitted. Thus, better time resolution could be realized. All kinetics experiments and most spectral determinations were performed using the stored energy mode.

Using a thiocyanate dosimeter, it was found that the dose for an 80 nsec pulse was \( 9.1 \times 10^{16} \) eV/cc of water in the standard reaction cell. By correcting for the increased electron density of
1,2-dichloroethane, it was calculated that the dose in DCE was $1.0 \times 10^{17}$ eV/cc for an 80 nsec pulse.

The long term (4 hr.) pulse stability was better than 10% for steady state pulses. The average dose delivered by an 80 nsec pulse was also found to change by less than 10% over four hours. However, pulse to pulse variations for an 80 nsec pulse were approximately 6%. This value was largely determined by the jitter of the pulse width timer. Pulse width varied by ±1 nsec about the nominal value for all pulses.

The rise and decay times of an electron pulse were each about 6 nsecs, independent of pulse width and mode of operation. Time profiles for two pulses are shown in Figure 1.

The position of the electron beam has been found to remain stable for extended periods of operation. Beam size and shape could be adjusted by means of the quadrupole magnets. The greatest electron density would be attained in a spot of 2mm diameter (the minimum beam diameter).

Position of the beam, its size and shape relative to the reaction cell, and the spectral purity of the electron beam determine the dose distribution within the reaction cell. It has been demonstrated\textsuperscript{26} that for the type of reaction cell used in this investigation, the radiation received is approximately uniform over the cell area in the plane perpendicular to the electron beam, as judged by the radiation darkening of a sheet of polyvinylchloride. It has also been determined that the absorbed dose along the electron beam does not vary by more than 10% from the value at the front of the cell.
Figure 1. Time profile of an 85 nsec pulse (A) and a 600 nsec pulse (B).
Boag\textsuperscript{27} has discussed the influence of non-uniform distributions of reactants on the measurement of rate constants. Under conditions of first order kinetics it is only necessary to have a uniform distribution of transients across the analyzing light beam. For the optical arrangements used in the experiments to be reported, this means that the distribution along the electron beam must be uniform. Pseudo first order rate constants for the distribution mentioned above will be in error by less than one per cent. With few exceptions, all the reacting systems investigated obeyed first order rate laws.

Determination of rate constants under second order conditions is affected by dose distribution both along and across the analyzing light beam. With the distribution described above, the error in measurement of a second order rate constant is less than \( \% \). That is less than other errors involved in the evaluation of second order rate constants by this method.

**Optical Detection**

The source of analyzing light for all experiments was an Osram high pressure xenon arc lamp, type XB0450. During steady state operation the lamp was operated at 20 volts, and 24 amperes current (i.e. 480 watts).

Output of the lamp could be increased by discharging large amounts (150 A) of current through it in pulses. Variable amounts of charge were stored in a capacitor bank and were discharged in parallel to the steady state power supply of the lamp. The maximum resulting increase in intensity was approximately a factor of 10.
to a factor of 40, depending on wavelength. The increase was greater toward the U.V.

A sample of the time profile of the lamp flash at 405 nm is shown in Figure 2. At oscilloscope sweep rates of 1 μsec/cm with vertical expansions of 20 mv/cm, the 10 μsec interval centered at the peak of the lamp flash appears flat. The start of this interval can be made to coincide with the electron pulse by means of a variable delay. Therefore, transient absorptions of first order processes can be observed under the condition of flashing the lamp, provided the half lifetime of the transient is of the order of 1 μsec or less.

A focusing lens is provided at the exit of the lamp housing. It was adjusted so the focus of the visible light was within the reaction cell. A shutter, which could be operated by remote control, and appropriate Corning glass filters were placed between the lamp and the reaction cell to prevent photolysis. Filters were also placed before the entrance slit of the monochromator to prevent second order components of light from reaching the photomultiplier tube. In many cases, this filter also helped to greatly reduce the amount of Cerenkov emission reaching the detector. The analyzing light was always passed through the cell at right angles to the electron beam.

Occasionally it was desirable to monitor two different wavelengths simultaneously. This was accomplished by reflecting the analyzing beam through the cell for two passes and onto a partially reflecting-partially transmitting mirror. The mirror was made of quartz and coated with chromium. The transmitted beam and the reflected beam were directed to two independent detection systems. Using this
Figure 2. Time profile of xenon flash at 405 nanometers.
arrangement, the effect of the formation of one absorbing transient on the yield of a different absorbing transient could be studied. A schematic diagram of this setup appears in Figure 3a.

Nearly all kinetic and spectral experiments were conducted using an optical arrangement similar to that in Figure 3a. The difference was that the partially reflecting-partially transmitting mirror was removed, along with the second monochromator and detector. The reacting systems in which this optical configuration was used were kept at the ambient room temperature (23 ± 1°C) throughout the course of the experiment.

In the determination of an activation energy, the temperature was controlled by means of a cryostat. The construction of the cryostat prevented reflecting the analyzing beam through the cell for a double pass. Therefore, whenever the cryostat was used, the detection system diagrammed in Figure 3b was employed.

The transient optical absorptions investigated were in the spectral range of 250 to 1100 nm. Three Bausch & Lomb monochromators, f 3.5, were used in these studies: a 33-86-25-07, a 33-86-25-02, and a 33-86-25-03. The 33-86-25-07 is a U. V.--visible grating monochromator with a range of 200-700 nm and a reciprocal linear dispersion of 7.4 nm/mm. The range of the 33-86-25-02 is 350-800 nm with a reciprocal dispersion of 6.4 nm/mm. The 33-86-25-03 was used in the near infrared. Its range is 700-1600 nm with a dispersion of 12.8 nm/mm. Calibration of each grating was accomplished by comparison of the observed wavelengths of known emission lines to their
Figure 3. (a) Schematic diagram of the double pass optical arrangement using a beam splitting mirror. (b) Schematic diagram of the single pass optical arrangement used in the determination of activation energies.
reported wavelengths. Oriel spectral lamps were used as the sources of the emission lines.

Upon exiting the monochromators, the light was detected by one of four photomultipliers. The RCA 7102 and 7200 photomultipliers, with S-1 and S-19 spectral responses, respectively, were used for the observation of transients with half-lifetimes greater than 1 µsec. The outputs of these detectors were amplified by Nexus FSL12 amplifiers, and were found to be linear in the range of 20 mV to 1 volt (into 93 ohms). 10-90% rise times for the detection systems using these photomultipliers were approximately 70 nsecs (essentially the rise time of the Nexus amplifier).

The RCA 1P28 and the HTV 196 photomultipliers were directly coupled to the 93 ohm transmission lines. By eliminating the amplifiers, the 10-90% rise times of the detection systems using these phototubes were less than 10 nsecs. These detectors were used to observe transients with half-lifetimes less than 1 µsec. They were linear in output from 0 volt to 1 volt into 93 ohm loads. The spectral response of the 1P28 was S-4 and that of the HTV 196 was S-1.

The linearity of the detectors was verified according to the following procedure. A square wave of constant amplitude was superimposed upon a D.C. signal that could be varied between 0 and 1 volt. The square wave was provided by a LED that was triggered by a Tektronix 114 pulse generator. The LED was placed in front of the optical window of the photomultiplier. The choice of a particular LED was governed by the spectral response of the detector being tested. D.C. signals were provided by the steady state light output
of the xenon lamp. The intensity of the light reaching the detector was varied by changing the aperture that the light passed through. This was accomplished by means of an iris diaphragm. Apparent variation of the amplitude of the square wave indicated the non-linearity.

The rise time of each detector was measured by observing the Cerenkov light emission of the electron pulse. The time profile of the Cerenkov emission follows the electron pulse. Therefore, its time profile is a rectangular wave with less than a 6 nsec rise time. The rise time of the detector systems using each of the photomultipliers was taken to be the apparent rise time of the Cerenkov emission.

The dual beam oscilloscope used in each experiment was either a Fairchild, Type 777, or a Tektronix, Type 7644. The bandpass of each scope, including its plug ins, was 100 MHz. The calibration of the oscilloscopes was tested during each experiment. A 0.000—1.000 volt precision voltage source was used to calibrate the gain of the vertical amplifiers and a Tektronix, Type 184, time mark generator was used to calibrate the time bases.

Materials

1,2-dichloroethane was reagent grade from Matheson, Coleman, and Bell. For most experiments it was purified in the following manner: Approximately 80 ml of concentrated sulfuric acid were added to 400 ml of dichloroethane and the mixture was vigorously shaken in a separatory funnel for one minute. The acid was removed and the DCE washed at least three times with demineralized, double distilled water from The Ohio State University Reagent Laboratory. It was
then washed twice with saturated aqueous solutions of sodium carbonate (various sources) prepared with water from the same source as that used in the washing. Following four or five washings with double distilled water, the DCE was then washed three times with triply distilled water. After drying over barium oxide (technical grade, Allied Chemical), it was then poured through a teflon stop-cock into an evacuated 500 ml glass storage bulb. After repeated freezing-evacuating-thawing cycles, approximately 50 ml were transferred into a small storage bulb by trap to trap distillation and were discarded. Finally, 250-300 ml were transferred by vacuum distillation to an evacuated 500 ml storage bulb containing freshly prepared Linde type 4A molecular sieves.

Occasionally, after being dried with barium oxide, the following steps were taken in addition to the procedure described above. The DCE was poured into a 1-l distilling flask and approximately 30 g of diphosphorous pentoxide (from Matheson, Coleman, and Bell) were added. After refluxing for several hours under a dry nitrogen atmosphere, it was distilled. The first 50 ml were discarded and the middle fraction of approximately 300 ml was treated as above.

The first two distillations of the triply distilled water were from acid dichromate solution and basic permanganate solution, respectively. For a carrier gas all three distillations used nitrogen that was first bubbled through distilled water. The purified water was stored in a stoppered, 1-l volumetric flask.

Bromodiphenylmethane, technical grade from Chemical Samples Co., was purified by vacuum sublimation. The pure sample was white, and
the crude sample was brown. The purified compound was stored
in vacuo.

Benzhydrol (99% pure, from Aldrich Chemical Co.) was purified
by recrystallization from a solution containing equal volumes of
triply distilled water and absolute ethanol (U.S.P., from Commercial
Solvents Corporation). Hot solution was poured onto the sample until
it was completely dissolved. The solution was filtered and the fil-
trate allowed to cool. The pure crystals that appeared upon cooling
were separated and dried by filtration in a buchner funnel. Further
drying was accomplished by pumping on a vacuum line. The sample was
stored in vacuo.

Chlorodiphenylmethane, practical grade from Matheson, Coleman,
and Bell, was purified by a series of fractional freezing cycles, fol-
lowed by treatment with activated charcoal.

Triphenylcarbinol (97%, from Aldrich Chemical Co.) was recry-
stallized from either DCE or cyclohexane (gold label, spectrophoto-
metric grade, from Aldrich). The procedure was the same as that
for benzhydrol with the additional step of adding activated charcoal
to the hot solution of dissolved sample.

Both triphenylmethyl bromide (J. T. Baker Chemical Co.) and tri-
phenylmethyl chloride (ICN-K & K Laboratories) were purified by
recrystallization from DCE according to the procedure outlined for
benzhydrol.

Dibenzyl mercury (from Alfa Inorganics) was purified by recryst-
allization from absolute ethanol (U.S.P. from Commercial Solvents
Corporation). The purification outlined for benzhydrol was followed. Dibenzyl sulfide, from Eastman, was used as obtained.

p-Terphenyl and biphenyl were both used as obtained. The zone refined samples from Aldrich were rated as 99.9+ % pure. The triethylamine, from J. T. Baker Chemical Co., was purified by distillation, under argon, into lithium aluminum hydride followed by distillation onto a freshly prepared potassium mirror in vacuo. After contacting the potassium mirror for several days, the solution was thoroughly degassed by repeated freezing-evacuating-thawing cycles. It was then distilled onto another freshly prepared potassium mirror for storage.

Tri-n-propylamine was obtained from two sources, the Aldrich Chemical Co. and ICN-K & K Laboratories. Tri-n-butyl amine was from Matheson, Coleman, and Bell as well as from ICN-K & K Laboratories. Both of these amines were purified using the following standard technique. The amine was dissolved in aqueous sulfuric acid and the pH adjusted to 4 or lower. The solution was then extracted with ethyl ether and the ethereal layer discarded. The resulting aqueous phase was made alkaline by the addition of a concentrated sodium hydroxide solution. The resultant biphasic mixture was separated to give the amine, which was subsequently dried with barium oxide and fractionally distilled, under argon, into storage vessels. It was then degassed by freezing-evacuating-thawing cycles and stored in vacuo. The tri-n-butyl amine was occasionally simply kept in a closed storage vessel.
Methanol-d and methanol-d$_4$, 99.5+ atom % D, both gold label grade from Aldrich Chemical Co., were used without further purification. Since they were sealed under nitrogen, they were transferred into evacuated storage vessels by pouring inside a glove box containing a dry nitrogen atmosphere. They were then degassed and stored in vacuo.

Cyclohexane used in the pulse experiments was research grade from Phillips Petroleum Company. The purity was rated at 99.99 mole percent with the most probable impurity being 2,4-dimethyl pentane. The cyclohexane was used without further purification.

Reaction Cells and Solution Preparation

Irradiation cells, from Pyrocell Inc., were made of fused quartz and had optical windows of high purity fused silica. The windows were resistant to darkening by irradiation. The internal dimensions of the irradiation cells were 8 mm in the direction of the electron beam, 20 mm along the analyzing light beam, and 12 mm in the vertical direction. The quartz walls were approximately 1 mm thick. Hence, the range of the incident electrons used in this investigation exceeded the dimension of the irradiation cell along their path.

The irradiation cell was only one part of the reaction cell. It was connected to the remainder of the reaction cell, which was made of Pyrex, by a graded seal. Design of the reaction cell was determined by the type of experiment in which it was to be used.

For spectral studies, the cell illustrated in Figure 4a was used. The reservoir was made from a 50 ml round bottom flask. The Teflon
Figure 4. Reaction cells used in pulse irradiation experiments: standard kinetic cell (a) and spectrum (b).
stopcock, from Kontes Glass Co., had a 0-4 mm bore. It could sustain a vacuum of $10^{-5}$ torr with its two Viton O-rings. The 9 mm Solv-Seal joint permitted the preparation of the cell on a vacuum line.

If the solute to be introduced into the cell was a liquid, it was always stored under an atmosphere of its vapor in a glass bulb. The weight of the glass bulb plus its contents was recorded. The storage bulb containing the solute, the reaction cell, which had been previously evacuated and weighed, and the storage vessel containing the solvent were joined to the vacuum manifold diagrammed in Figure 5. After evacuating the interconnecting tubing, the stopcocks between the reservoir and the solute were opened and the reservoir was immersed in liquid nitrogen. Approximately the desired amount of solute was vacuum distilled into the reservoir and the stopcock on the storage bulb was closed. The valves between the reservoir and the solvent were then opened and the solvent was also vacuum distilled into the reaction cell.

The storage bulb from which the solute was distilled was weighed again on an electric analytical balance. The amount of solute transferred was then obtained from the difference in weight of the storage bulb and its contents before and after distillation. This quantity was determined to within ±0.1 mg. Similarly, the amount of solvent that was transferred was defined by the difference in weights of the prepared cell and the evacuated cell, taking care to account for the weight of the solute. The reaction cell was weighed to within ±0.2 g on a triple beam balance.
Figure 5. Schematic diagram of the vacuum manifold upon which the reaction cells were filled.
If the solute was a solid, the desired amount was weighed on an electric analytical balance. It was transferred into the reservoir of the cell by pouring through the bore of the stopcock by means of a funnel. The cell was then evacuated and weighed. An amount of solvent was then vacuum distilled into the cell according to the procedure described in the preceding paragraphs. The amount of solvent that was transferred was evaluated by weight difference.

The standard kinetic cell, illustrated in Figure 4b, consists of two reservoirs joined by a pipette with Teflon stopcocks at each end. The construction of this cell permits measured volumes of a solution containing a reactant to be added, through the pipette, to the irradiation section of the cell. Thus, this cell was used in experiments designed to study the effects of changing reactant concentration on the rate of reaction. The reservoir joined to the irradiation cell contained the solution of the carbonium ion precursor and the second reservoir contained the solution of the nucleophile. The bulb used to hold the solution of the nucleophile was always filled first. Each of the solutions was prepared according to the same procedure that was used for the filling of the spectrum cell.

The standard kinetic cell was also used in experiments designed to define yield curves and to obtain rate constants for the formation of organic cations. In those experiments, a solution of the precursor to the cation was prepared in the second reservoir and pure solvent was added to the bulb joining the irradiation cell.

Occasionally it was necessary to keep one solute at constant concentration while varying the concentration of a second solute. The
modified kinetics cell, illustrated in Figure 6, was used in these instances.

The solute of constant concentration is defined as solute a and the solute of variable concentration is defined as solute b. Solute b was weighed and then placed in the appendage added to the standard kinetic cell. The appendage was then evacuated and its valve closed. A solution of solute a was prepared in the reservoir joined directly to the irradiation cell. The preparation followed the procedure outlined for filling the spectrum cell. A measured volume of the solution containing a was then added to the second reservoir through the pipette. This volume was approximately one-half the initial volume. After opening the valve of the appendage, solute b was dissolved in this solution. The concentration of solute b contained in this reservoir was defined by the amount of b and the volume of solution added to the reservoir. The concentration of solute a was the same in both reservoirs. By adding volumes of the solution containing both solutes to the irradiation section of the cell, the concentration of b in that section could be varied while the concentration of a remained constant.

In most experiments the reaction cells were kept at the ambient temperature of the accelerator facility, 23 ± 2°C. However, an experiment for determining the activation energy of a formation process required the temperature control provided by a cryostat.

The cryostat was a brass box insulated with one inch thick Styrofoam on its exterior. Two holes, which were aligned on opposite faces of the box, were covered with evacuated quartz cuvettes. The
Figure 6. Modified kinetic cell.
cuvettes served as optical windows for the analyzing beam. An electron window of thin copper foil was situated on one side of the cryostat so that the electron beam would intersect the analyzing beam at a right angle.

The kinetic cell was mounted to the cryostat by means of a $\frac{34}{45}$ standard taper. An outer taper was an integral part of the top of the cryostat. It was located so that the axis through its center passed at a right angle through the intersection of the analyzing beam and the electron beam. A Pyrex inner taper was blown onto a standard kinetic cell between the irradiation cell and its reservoir, as shown in Figure 4b. The distance between the irradiation cell and the taper was chosen to ensure proper positioning of the irradiation cell with respect to the electron beam and the analyzing beam.

Cooling was achieved by blowing cold dry nitrogen into the cryostat. The nitrogen was cooled by passing it through a copper coil immersed in liquid nitrogen. Temperature was regulated by the rate of flow of nitrogen. Dry nitrogen kept at room temperature was blown across the optical windows to prevent fogging.

Temperatures were regulated by the rate of flow of cold nitrogen. They were measured by means of a copper-constantan thermocouple and a Leeds and Northrup potentiometer. The reference junction was kept at 0°C and the test junction was cemented to the irradiation cell. In order to ensure equilibrium, each temperature was maintained for several minutes before irradiation. Temperatures varied by less than ±0.5°C for each irradiation period.
Since the volumes of the reservoirs greatly exceeded the volumes of the irradiation cells, stable irradiation products could be diluted by simply tipping the reaction cell. However, no effects of stable radiation products were observed in the experiments reported in this work.

The radiation cells and all storage vessels were cleaned as follows: The glassware was first rinsed repeatedly with 1,2-dichloroethane. Absolute ethanol was used to remove the DCE and to provide further cleaning action. The glassware was then washed repeatedly with triply distilled water. Finally, it was placed in an annealing oven over night in order to dry, and to pyrolyze any residual organic substances.

Data Analysis

Data from the pulse radiolysis experiments were always obtained in the form of Polaroid photographs of oscilloscope traces. Either Type 107 film, 3000 speed, or Type 410 film, 10,000 speed, was used, depending on the intensity of the trace that could be obtained. The image size to the oscilloscope grid on the Polaroid film was 83 mm x 63 mm. In order to obtain the most easily and accurately read data, maximum expansions were used on the scope in order to fill the linear region of the CRT with that portion of the trace that was of interest.

The data were analyzed directly from the Polaroid photographs for spectral determinations. For kinetic experiments, the Polaroid oscillograms were always copied on 35 mm, ASA 125, black and white negative film. Enlargements, 8" x 10", were made from the negatives,
yielding a minimum of 3 x linear expansion. The exact magnitude of the expansion depended upon the fraction of the original Polaroid that contained the data to be analyzed. The acceptability of a particular enlargement was judged by the parallelism and perpendicularity of the grid lines.

Figure 7 shows two representative oscilloscope traces. The oscilloscope was actually triggered for two sweeps each time the linac was fired once. The first sweep occurred before the linac was triggered and, if the lamp was flashed, before the lamp flash. Therefore, it represents the steady state light intensity passing through the irradiation cell. The second trace was begun just before the electron pulse had begun and sufficiently long after the beginning of the lamp flash that a plateau in its intensity had been reached. The portion of the trace preceeding the electron pulse represents the amount of light, \( I_0 \), transmitted through the unirradiated cell.

Virtually all transient absorptions were sufficiently small so that expanding them to fill the CRT put the base line, or first sweep, off the scale. The relative value of \( I_0 \), which is related to the distance between the base line and the \( I_0 \) line, could not be directly determined from these pictures if they were taken on the Fairchild 777 oscilloscope. A sampling digital volt meter was then used to determine the value of \( I_0 \). This unit, designated the "\( I_0 \) meter", could sample the amplitude of a signal over a one microsecond interval. The location of the interval could be varied over a four millisecond range, in four steps. The end of the 1 \( \mu \)sec sampling interval was placed 200 nsec before the start of the electron pulse.
Figure 7. Two typical oscilloscope traces showing formation (A) following the pulse and decay (B) following the pulse.
for all experiments reported herein. The $I_o$ meter was capable of reading within ± 1 millivolt.

Since the vertical plug-in of the Tetronix 7844 was a differential amplifier, the traces could be precisely displaced along the ordinate. Therefore, a particular grid mark could be adjusted to correspond to an expected value of $I_o$. The actual values of $I_o$ could be determined from the distance between the initial portion of the trace and the designated grid line. Since the $I_o$ meter yielded values of $I_o$ directly, it was used for nearly all experiments, regardless of the scope being used.

The kinetically significant variables that could be related to the oscilloscope pictures were time and concentration. Time was measured directly from the photographs. The relative intensity of the light that was absorbed, $I_a$, could also be measured directly. In order to relate $I_a$ to concentration, Beer's law was applied.

$$D_t^\lambda = \log_{10} \frac{I_o^\lambda}{I_o^\lambda - I_a^\lambda} = \epsilon^\lambda [C]^d$$

$I_o$ and $I_a$ were obtained from the data and $d$ represents the distance that the light traverses through the absorbing solution. $\epsilon$ is decadic molar extinction coefficient, a constant at any particular wavelength in these experiments. Since most kinetic treatments presented in this work required only relative concentrations, knowledge of the value of $\epsilon$ was normally not necessary.

Because of the transient nature of the absorbers studied in this work, the validity of Beer's law was not directly tested (i.e. plots
of concentration vs. O.D. were not made). However, the applicability of this absorption law to similar pulse irradiated systems has been carefully examined. It was shown that the law is valid providing $\epsilon$ is nearly constant over the bandpass of the monochromator. The spectra of the transients that were the subject of this investigation indicate that the extinction coefficients in the 10 nm interval centered about the absorption maxima are nearly constant. Since the bandwidth from the monochromators was typically less than 4 nm, Beer's law was valid.

Measurements of distances representing $I_a$ for all spectral determinations were made with dial calipers. The accuracy was $\pm 0.001''$. For all kinetic determinations, distances corresponding to time and relative values of $I_a$ were measured from the 8" x 10" enlargements with a Hewlett Packard calculator digitizer, Model 9107A. The digitizer consists of a cursor, a platen, and a mainframe. The cursor is an electro-magnetic transmitter, operating at 3 kHz. The platen, a digitizing surface, acts as a receiving system. Conversion of the received information into coordinates describing the position of the cursor occurs in the mainframe.

The kinetic curves were digitized by tracing over them with the hand held cursor. Each measurement was made with an accuracy of $\pm 0.01$ inch. Distances were stored in terms of Cartesian coordinates with respect to a user designated origin. Storage capability was provided by a Hewlett Packard Model 9101A Extended Memory. The data were normally operated on by the appropriate data reduction programs that were stored in the 9101A and were executed by the Hewlett Packard calculator, Model 9100B.
RESULTS AND DISCUSSION

Arylcarbonium ions and aromatic radical cations were observed in 1,2-dichloroethane and cyclohexane. The rate constants for the formation of these ions in dichloroethane have been determined and the mechanism of formation has been investigated.

The reactivities of the carbonium ions in several electrophilic reactions were also determined.

Observation of Molecular Ions in Dichloroethane

The two radical cations that were studied in this investigation are the biphenyl radical cation, \( \text{Ph}_2^+ \), and the para-terphenyl radical cation, \( \text{p-Ph}_3^+ \). Observation and identification of these molecular ions in pulse irradiated solutions of 1,2-dichloroethane have been previously reported.\(^1\)

Pulse irradiation of degassed dilute solutions (5 x 10\(^{-2}\) - 10\(^{-3}\)) of biphenyl in DCE produces an absorption band at 380 nm and a weaker band at 690 nm.\(^1\) Below 400 nm there is a small contribution due to a long lived species. The decay of the absorption above 400 nm is independent of wavelength, indicating that only one transient is responsible for the absorption. That transient was identified as \( \text{Ph}_2^+ \). Assignment of the absorption to the biphenyl cation was accepted without further testing in this investigation. Because of the absence of overlapping absorptions at the 690 nm band, this spectral region was
monitored in order to follow the concentration of the cation.

Pulse irradiation of $4.3 \times 10^{-2}$ M p-terphenyl in a degassed solution of DCE produces the p-terphenyl cation.\textsuperscript{11} It exhibits a U.V. absorption band at 455 nm and a near I.R. absorption band with a peak at 965 nm. Below 400 nm a species with a much longer lifetime than p-Ph$_3^+$ is also absorbing. For the kinetic studies reported in this work, the concentration of p-Ph$_3^+$ was followed by monitoring the absorption at either 455 nm or 960 nm. Therefore, there were no problems associated with overlapping absorptions due to other transients derived from the precursor compound. The assignment of the absorption to the p-terphenyl cation was also accepted without further testing.

The trityl, Ph$_3$C+, the benzhydryl, Ph$_2$CH+, and the benzyl, PhCH$_2$+, cations may be produced from a variety of precursor compounds in pulse irradiated solutions of DCE. Their identification, as outlined in the Introduction, is quite unequivocal. The trityl cation has absorption peaks at 415 nm and 439 nm. The benzhydryl cation and the benzyl cation have absorption maxima of 445 nm and 363 nm, respectively, in DCE. Although no structure determinations were performed, the absorption at 363 nm was assigned to the benzyl cation rather than to the tropylion ion, C$_7$H$_7^+$ . The absorption spectrum of the tropylion ion is known,\textsuperscript{32} and it does not have a maximum at 363 nm.

For most experiments the concentrations of the carbocations were followed by observing the changes in optical density at their absorption maxima. However, the possibility of overlapping absorptions had to be investigated for each precursor compound, since absorbing transients other than carbonium ions were likely to be formed. Furthermore,
in determining the reactivity of these carbonium ions with various nucleophiles, the occurrence of interfering absorptions from transients derived from the nucleophile also had to be investigated.

**Observation of Carbonium Ions in Cyclohexane**

Irradiation of a $2.7 \times 10^{-2}$ molar solution of dibenzylmercury in air saturated cyclohexane, using 80 nsec electron pulses, results in the spectra shown in Figure 8. The wavelength of the absorption maxima and the shapes of the bands correspond to the benzyl cation.

Since the cyclohexane was saturated with air, the benzyl anion was not produced in these solutions. Both the electron, which is responsible for the formation of carbanions in irradiated solutions, and the benzyl carbanion react rapidly with oxygen. Studies in tetrahydrofuran and ethylenediamine indicate that the benzyl carbanion will not be formed in air saturated solutions.

The decay characteristics of the absorption band in the region of 340 nm to 420 nm indicate that there is no spectral overlap due to other absorbers. Thus, changes in the concentration of the benzyl cation could be followed by monitoring the optical density at its absorption maximum. Transients produced from the solvent did not absorb above 320 nm.

The spectra in Figure 9a indicate the absorptions due to the transients produced upon pulse irradiation of a $2.8 \times 10^{-2}$ molar solution of bromodiphenylmethane in cyclohexane saturated with air. The decay characteristics indicated that three species were present. The benzhydryl cation, with $\lambda_{\text{max}} = 445$ nm, was clearly present.
Figure 8. Optical absorption spectra of the benzyl cation formed in a $2.7 \times 10^{-2}$ M solution of dibenzylmercury in cyclohexane. Spectrum (a) was obtained at the end of an 80 nsec pulse. Spectrum (b) was obtained 250 nsec after the pulse.
Figure 9. (a) Transient optical absorption spectra produced upon irradiating a $2.8 \times 10^{-2}$ M solution of bromodiphenylmethane in cyclohexane. Spectrum 1 was obtained at the end of the pulse and spectrum 2 was obtained 1 μsec after the pulse. (b) Difference spectrum obtained by subtracting spectrum 2, normalized to spectrum 1 at 445 nm, from spectrum 1.
The absorption band due to the benzhydryl cation was subtracted from the time zero spectrum with normalization at 445 nm. The resulting difference spectrum is shown in Figure 9b. This spectrum is a composite of two different absorption bands from a long lived species with $\lambda_{\text{max}}$ near 335 nm and a shorter lived species with $\lambda_{\text{max}}$ less than 315 nm. The band at 335 nm is most likely the benzhydryl radical, with a reported absorption maximum of 335-339 nm. The species absorbing below 315 nm has not been identified. Overlap of the band from the radical with the absorption due to the cation is negligible above 425 nm. Therefore, kinetic data obtained at the absorption maximum would be free of complications due to overlapping absorptions.

The transient optical absorption spectrum produced upon pulse irradiation of a $1 \times 10^{-2}$ molar solution of trityl bromide in air saturated cyclohexane can be attributed to the trityl cation and the triphenylmethyl radical. The composite spectrum is essentially the same as that obtained by Capellos and Allen upon pulse radiolysis of $10^{-3}$ molar triphenylmethanol in cyclohexane. They also successfully produced the trityl cation in cyclohexane and a number of other solvents using trityl chloride as the precursor.

Capellos and Allen observed that the yield of the trityl cation produced from the carbinol precursor was independent of concentration, above $10^{-4}$ molar of carbinol. This yield was only approximately one-half the value of the yield of the free ions produced in cyclohexane, as determined by field clearing experiments. However, the yield of trityl cations when as little as $10^{-3}$ molar trityl chloride was used as precursor, was essentially that of the free ions.
They suggested the following mechanism to account for their observations. The formation of the trityl cation in hydrocarbon solvents results from a proton transfer from the cation of a hydrocarbon solvent to the precursor, rather than an electron transfer, as suggested in the Introduction. (Providing the charge transfer process is rate limiting, the two processes are kinetically indistinguishable.) The overall reaction was represented as

\[
\text{Ph}_3\text{CX} + \text{RH}^+ = \text{Ph}_3\text{C}^+ + \text{R} + \text{HX}
\] (8)

The low yield of carbonium ion when the carbinol was used as precursor was explained in the following terms: When X = OH, "the water molecule that is formed sometimes back reacts with the carbonium ion so that the ion is not seen, while the analogous reaction does not take place with the HCl formed in the case of the chloride."

The kinetics and mechanism of the formation of the three arylicarbonium ions in cyclohexane were not investigated in the experiments reported herein. However, the plausibility of the explanation of the observed yields offered by Capellos and Allen can be examined. If the elementary steps for the formation process may be represented as

\[
\begin{align*}
\text{Ph}_3\text{CX} + \text{RH}^+ & \longrightarrow \text{Ph}_3\text{CXH}^+ + \text{R} \\
\text{Ph}_3\text{CXH}^+ & \longrightarrow \text{Ph}_3\text{C}^+ + \text{HX} \\
\text{HX} + \text{Ph}_3\text{C}^+ & \longrightarrow \text{Ph}_3\text{CXH}^+
\end{align*}
\] (9) (10) (11)
then the reduced yield in the case of the carbinol precursor would have to be accounted for in terms of a corresponding yield of \( \text{Ph}_3\text{COH}_2^+ \). By estimating the rate constants for Reactions (9), (10), and (11), the amount of carbonium ion lost in the back reaction can be estimated.

Capellos and Allen observed the formation of the trityl cation following the pulse when trityl chloride was used as precursor. They determined that the rate constant for the charge transfer process was \( 5.3 \times 10^9 \).

As will be shown in the following section, the rate constants for the formation of the trityl cation in DCE have been determined for both the chloride precursor and the alcohol precursor. The two rate constants differed by less than 30%. If it is assumed that the corresponding rate constants differ by approximately the same amount when cyclohexane is used as solvent, the half-time of formation with \( 10^{-4} \) M carbinol used as precursor can be approximated as \( 1 \times 10^{-6} \) sec. Therefore, the halftime for Reaction (10) must be less than \( 1 \times 10^{-6} \) sec.

The reactions of the benzyl cation and the benzhydryl cation with water, in the non-polar solvent DCE, have been examined and the appropriate rate constants obtained. The second order rate constants were \( 2 \times 10^7 \) M\(^{-1}\) sec\(^{-1}\) for the benzyl cation and \( 1 \times 10^6 \) M\(^{-1}\) sec\(^{-1}\) for the benzhydryl cation. It is expected that the trityl cation would react with water with a rate constant equal to or less than \( 10^6 \) M\(^{-1}\) sec\(^{-1}\). It is assumed that this rate constant would not change appreciably in cyclohexane. Based on their published values for the yield and the doses that they used, the maximum concentrations of the carbonium ion formed were approximately \( 1.4 \times 10^{-7} \) molar. Thus,
the maximum concentration of water formed was also $1-4 \times 10^{-7}$ molar. Therefore, the minimum half-time for Reaction (11) would be about 2 sec under the conditions of the experiments conducted by C & A. The effect of the back reaction would be negligible according to the reaction scheme above.

In the treatment outlined above, it was assumed that the water molecule and the carbonium ion were freely diffusing. The objection could be raised that the water molecule and the carbocation are formed as a complex. The complex may then dissociate to form the free cation or it may revert to the protonated carbinol at a rate not limited by diffusion. The steps in this representation would be

\[
\text{Ph}_3\text{CX} + \text{RH}^+ \longrightarrow \text{Ph}_3\text{CXH}^+ + \text{R}^+ \quad (9)
\]

\[
\text{Ph}_3\text{CXH}^+ \longrightarrow \text{Ph}_3\text{C}^+, \text{XH} \quad (12)
\]

\[
\text{Ph}_3\text{C}^+, \text{XH} \longrightarrow \text{Ph}_3\text{CXH}^+ \quad (13)
\]

\[
\text{Ph}_3\text{C}^+, \text{XH} \longrightarrow \text{Ph}_3\text{C}^+ + \text{XH} \quad (14)
\]

This mechanism is not sufficient to explain the decreased yield from the carbinol precursor. At sufficiently long times, determined by the values of the rate constants, all the positive charge would be scavenged to form the carbonium ion.

Reactions competing for RH$^+$ or Ph$_3$CXH$^+$ could conceivably reduce the concentration of carbonium ion formed. However, the effect of competition for RH$^+$ would decrease as the concentration of the precursor compound was increased. Since Capellos and Allen found that
the yield was independent of carbinol concentration above $10^{-4}$ molar, competition for RH$^+$ cannot satisfactorily account for the low yield.

Competition for Ph$_3$CXH$^+$ would be sufficient to lower the yield of the cation.

$$\text{Ph}_3\text{CXH}^+ + Q \rightarrow Y \quad (15)$$

Reaction (15) could be a reaction with counter ion, impurity, or precursor. The fraction of Ph$_3$CXH$^+$ forming Y would be independent of precursor concentration, as observed by C & A. However, if this competition is introduced into the mechanism, it is not necessary to incorporate the back Reactions, (11) or (13), into the mechanism to explain the lower yield of carbonium ions than of the free ions produced in cyclohexane.

In summary, the reaction of the trityl cation with water does not appear to be sufficient or necessary to explain the low yield of trityl cation from triphenylmethanol. A parallel reaction of Ph$_3$CXH$^+$, Reaction (15), would result in lower yields. The results indicate that the rate of this reaction would have to be comparable to the rate of the carbonium ion forming step with the alcohol precursor, and negligible compared to the rate of the carbonium ion forming step with the chloride precursor.

Since a similar reduction in yield is encountered when a carbinol precursor is used in DCE, a more detailed study of this phenomenon will be described in a following section. The mechanistic implications will be discussed.
Capellos and Allen suggested that the trityl cation was formed in hydrocarbon solvents as a result of a proton transfer from the solvent cation. However, radical cations derived from the solute most probably result from an electron transfer from the solute to the radical cation of the hydrocarbon solvent. It would be reasonable to expect that in the same solvent, both radical cations and carbonium ions derived from the solute would be formed according to similar primary mechanisms. The electron transfer mechanism could be applied to both hydrocarbon solvents and other solvents in which a proton transfer is impossible. For example, the formation of the trityl cation in pulse irradiated solutions of trityl chloride in carbon tetrachloride or carbon disulfide\(^{22}\) could be explained in terms of electron transfer.

If the carbonium ions are formed as a result of electron transfer, a simple, empirical method may be used to predict the formation of a carbonium ion from various precursor compounds in a particular solvent. Gas phase data are frequently available that give the appearance potential of a carbonium ion from various precursor compounds. This is the energy necessary for the following reaction to occur in the gas phase

\[
P_X \longrightarrow P^+ + X^- + e^- \tag{16}
\]

where PX is the precursor compound and P\(^+\) the carbonium ion. The energetics for this reaction are the same if the P-X bond is broken first and the resulting radical, P\(^-\), is then ionized
Occasionally, the appropriate bond energies and ionization potentials are known, from which the appearance potential can be derived.

If the ionization potential of the solvent exceeds the appearance potential of the carbocation, it is likely that the carbonium ion will be formed by electron transfer.

\[ \text{S}^+ + \text{PX} \rightarrow \text{S} + \text{P}^+ + \text{X} \]  \hspace{1cm} (19)

The application of this prediction to liquid systems is feasible only when the solvation energy of the products of Reaction (19) equals or exceeds that of the reactants. The severity of the approximations is recognized; however, appropriate thermodynamic data associated with carbonium ions in the liquid phase are not available.

The gas phase ionization potential of cyclohexane has been determined to be 9.8-10.5 eV.\textsuperscript{37} Based upon the reported ionization potential of the benzhydryl radical\textsuperscript{37} and the bond dissociation energy of the bromine atom bound to the appropriate carbon atom in bromodiphenylmethane,\textsuperscript{38} the gas phase appearance potential of the benzhydryl cation from this precursor is 9.23 eV. The ionization potential of the benzyl radical is 7.76 eV.\textsuperscript{37} The dissociation energy of the first benzyl group from the mercury atom in dibenzylmercury is expected to be 2 eV or less. Therefore, the appearance potential of PhCH\textsubscript{2}+ from dibenzylmercury is less than 9.76 eV. The approximate method outlined
above predicts that cyclohexane is an acceptable solvent for generating the benzhydryl cation from bromodiphenylmethane and the benzyl cation from dibenzylmercury. The data presented earlier indicate that this is the case.

Other considerations must be made in addition to the gas phase thermodynamic data when choosing precursor-solvent pairs. The precursor must be soluble in the solvents. If the reactivity of the carbonium ion is to be studied, the carbonium ion should not be spontaneously generated in the solution. Furthermore, the carbonium ion should not react with the solvent at an appreciable rate, as it would with alcohols.

Cyclohexane meets all these criteria for the systems studied thus far. Although the reactivity of arylcarbonium ions in cyclohexane has not been examined, the results described in this section indicate that it would be a routine matter to do so. Furthermore, the transient absorption spectrum produced upon irradiation of aerated cyclohexane is essentially free of absorption above 315 nm and has much less intense absorption in the 250 nm-315 nm region than the spectrum produced from dichloroethane. Future attempts to generate allylic type carbonium ions may be less complicated with cyclohexane as solvent than with DCE, the solvent used exclusively for the remaining experiments described in this dissertation.

Formation of Molecular Cations in 1,2-Dichloroethane

Molecular cations were formed after the electron pulse in solutions of 1,2-dichloroethane and appropriate concentrations of precursor compounds. The concentration ranges of precursors over
which formation could be observed were determined by the extinction coefficients of the resulting molecular cations and by the rate constants for the cations' formation. For a given dose and formation rate constant, the smallest concentration of precursor compound necessary to produce a detectable amount of cation was inversely proportional to the extinction coefficient of the cation. The minimum usable concentration of precursor was also found to decrease as the formation rate constant increases, but not in a simple manner. The maximum concentration of precursor was always chosen so the half time for the formation of the molecular ions was approximately 50 nsecs. This half time was found to be the shortest practical limit for accurate treatment of data obtained in these experiments.

The number of solute cations formed is linear in dose. Because of its higher beam current, a given dose can be delivered to the irradiation cell in a shorter period of time when the stored mode is used than when the steady state mode is used. A larger fraction of solute cations will be formed after a stored energy pulse than after a steady state pulse of the same dose, providing the half-time of formation is comparable to or exceeds the duration of the shorter pulse. Since only the portion of the oscilloscope trace following the electron pulse was analyzed, a larger portion of the oscilloscope trace could be analyzed when the stored mode was used. The electron pulses for all experiments involving formation kinetics were 40-80 nsecs in duration (stored energy mode).

In all but one experiment, there were two kinetic regimes in the formation process, a fast increase in absorption during the pulse.
followed by a slower formation process. The slower formation process was always found to fit a first order rate law. The first half-times for the natural decay of the cations derived from the solute were normally about 10 μsecs. Half-times for formation processes were always adjusted to be considerably less than those for the decay process. Therefore, decay of the cation was negligible during the time of its formation. The decay appears as a plateau in the oscillograms obtained in the study of formation kinetics. A typical example is shown in Figure 7.

The formation kinetics of each carbonium ion and aromatic radical cation will be discussed individually.

Benzhydryl Cation. Formation of a carbonium ion in DCE after the electron pulse was first observed for a solution of bromodiphenylmethane. It is assumed that the carbonium ion is formed as a result of dissociative ionization of the precursor compound. The precursor compound is ionized as an indirect result of irradiation, presumably by electron transfer to a cationic species derived from the solvent. The identification of the solvent species responsible for the ionization has not been positively made. However, in similar systems involving the appearance of aromatic radical cations, it has been suggested that the species may be the solvent cation radical, \( S^+ \). For the following discussion, \( S^+ \) will be used to represent either the solvent radical cation or the appropriate cationic fragment species derived from the solvent. \( S^+ \) may be in either the ground state or an excited state.
The reaction

\[ S^+ + \text{Ph}_2\text{CHBr} \rightarrow \text{Ph}_2\text{CH}^+ + \text{Br}^- + S \]  \hspace{1cm} (20)

will be considered as the only reaction responsible for the formation of the carbonium ion. The first approximation made in the extraction of the formation rate constant was that there were no competing reactions for \( S^+ \). This simplified mechanism may be described by the reactions

\[ e^- + S \rightarrow S^+ + 2e^- \hspace{1cm} t \leq p \]  \hspace{1cm} (21)

\[ S^+ + PX \rightarrow S + P^+ + X^- \hspace{1cm} t \geq 0 \]  \hspace{1cm} (22)

Since the concentrations of the precursor compounds, \( PX \), were always much larger than the concentrations of any transients produced in the solvent, the concentration of the precursor was essentially constant following any particular pulse. The pulse duration is represented by \( p \) in Reaction (21). The solutions to the differential equations resulting from this simplified mechanism appear in Appendix A. They indicate that if this mechanism applies, a plot of \( \ln(D_\infty - D_t) \) against time will be a straight line for times after the pulse. Straight lines were obtained, from the slopes of which first order rate constants for Reaction (22) were obtained. An example of a plot of \( \ln(D_\infty - D_t) \) vs. time for the formation of \( \text{Ph}_2\text{CH}^+ \) from bromodiphenylmethane is shown in Figure 10. The experimental first order rate constants are linearly dependent on the concentration.
Figure 10. Plot of $-\ln(D_e - D_i)$ against time for the formation of the benzhydryl cation from bromodiphenylmethane. The solid circles are experimentally determined points.
of the precursor compound. Figure 11 is a plot of the observed first order rate constants against the concentration of bromodiphenylmethane. The slope of this graph is the second order rate constant of Reaction (22). Its value is $1.6 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, probably the diffusion limited rate constant for this reaction.

Calculation of the diffusion limited rate constant from the Smoluchowski equation gives $k_{\text{diff}} = 9 \times 10^9$ at $24^\circ\text{C}$. This calculation is shown in Appendix B. There is good agreement between the two values considering the approximate nature of the calculation. The rate constants for the reactions of arylcarbonium ions with halide ions are also believed to be diffusion limited. These rate constants are all approximately $6 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. They are expected to be higher than the rate constants for the formation of the carbonium ions since they are for the reaction between oppositely charged species. Furthermore, the ionic radius of the solvent cation probably exceeds the radius of the halide ion.

The linear dependence of the observed first order rate constants on the concentration of the precursor compound suggests that the rate limiting step for the formation of the benzhydryl cation from bromodiphenylmethane is the electron transfer, Reaction (22). If the observed first order rate constants were independent of precursor concentration, the occurrence of an intermediate radical cation, $\text{Ph}_2\text{CHBr}^+$, would have been suggested. The rate limiting step for the formation would then have been the dissociation of the parent ion.

Only one wavelength was monitored in each kinetics experiment. In order to establish that the increase in absorption at 445 nm,
Figure 11. Plot of the pseudo first order rate constant, $k^*$, for the formation of the benzhydryl cation from bromodiphenylmethane vs. the concentration of bromodiphenylmethane.
following the electron pulse, was actually due to the formation of the benzhydryl cation, the absorption spectrum was taken at several times after the pulse. These spectra are shown in Figure 12. It is quite clear from the spectra that only one species is responsible for the formation at 445 nm and that it is indeed the benzhydryl cation.

Formation rate curves were also observed when \(0.5-1.7 \times 10^{-2}\) molar solutions of benzhydrol, \(\text{Ph}_2\text{CHOH}\), were irradiated. The curves differed from those obtained when bromodiphenylmethane was used as a precursor. After the initial rapid increase in absorption during the pulse, there was a decay followed by a much longer period of formation. The optical densities were smaller than those obtained when the analogous experiment was conducted with the bromodiphenylmethane solutions. Nevertheless, the slow formation was linearized by a plot of \(\ln(D_\infty - D_t)\) against time. The slopes of these plots were plotted against the concentration of precursor compound. Straight lines resulted, whose slopes are the second order rate constants for the electron transfer reaction. The rate constant is \((4.0 \pm 1.0) \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}\). Figure 13 shows the graph from which this rate constant was obtained.

The error in the rate constant for the formation from the carbinox precursor exceeded the error in the determination of the rate constant from the bromide precursor because only a smaller portion of the formation rate curves could be analyzed.

Chlorodiphenylmethane also forms the benzhydryl cation when DCE solutions of the compound are pulse irradiated. A spectrum of the transients produced in the irradiated solutions are shown in Figure 14. The amount of the carbonium ion formed depends upon the concentration
Figure 12. Optical absorption spectra of the benzhydryl cation formed in a $2 \times 10^{-4}$ M solution of bromodiphenylmethane in 1,2-dichloroethane. Spectrum A was obtained 140 nsec after the 80 nsec pulse and spectrum B was obtained 1.3 $\mu$sec after the pulse.
Figure 13. Plot of the pseudo first order rate constant for the formation of the benzhydryl cation from benzhydrol against the concentration of benzhydrol.
Figure 14. Optical absorption spectrum of the benzhydryl cation formed in a $9 \times 10^{-2}$ M solution of chlorodiphenylmethane in 1,2-dichloroethane. The spectrum was obtained at the end of a 600 nsec electron pulse.
of chlorodiphenylmethane, as will be discussed in a later section.
However, the optical density at 445 nm does not increase after the
electron pulse, as it does for the solutions of benzhydrol and bromo-
diphenylmethane. Therefore, the formation rate constant could not be
evaluated in the manner previously described.

**Trityl Cations.** The trityl cation was formed in pulse irradiated
solutions of trityl bromide, trityl chloride, or triphenylmethanol in
DCE. The cation was formed following the electron pulse in all three
instances. The resulting formation curves, obtained at the 439 nm
absorption maximum, were linearized by plots of ln(D_\infty - D_t) vs. time.
Second order rate constants were obtained according to the procedure
described for the benzhydrol cation.

Gavlas has determined the formation constants for solutions of
triphenylmethanol and trityl bromide. They are 5.7 x 10^8 M^{-1} sec^{-1}
and 8.4 x 10^9 M^{-1} sec^{-1}, respectively. Re-examination of his data
indicated that the trityl bromide solutions behave similarly to benz-
hydrol bromide solutions. Likewise, the triphenylmethanol solutions
behaved as the benzhydrol solutions. That is, for a given half-time
of formation, the optical density due to the trityl cation absorption
was much greater when the bromide precursor was used than when the car-
binol was used. The oscillograms of the solutions containing the
carbinol precursor also showed a small initial decay before the slow
formation process.

The plot of first order formation rate constants against the con-
centration of trityl chloride appears in Figure 15. The slope of this
plot is 4.0 x 10^8 M^{-1} sec^{-1}, the second order rate constant for the
Figure 15. Plot of the pseudo first order rate constant for the formation of the trityl cation from trityl chloride against the concentration of trityl chloride.
formation of the trityl cation from the chlorinated precursor compound. The characteristics of the formation curve were the same as those described for solutions of benzhydrol and triphenylmethanol.

**Benzyl Cation.** The benzyl cation was formed following the electron pulse in dichloroethane solutions containing $1.5 \times 10^{-4}$ M to $7.5 \times 10^{-4}$ M dibenzylmercury. This was indicated by the increase in optical density at the 363 nm maximum of the benzyl cation absorption. By treating the data in the manner previously described, the second order rate constant for the benzyl cation formation for dibenzylmercury has been determined to be $1.3 \times 10^{10}$ M$^{-1}$ sec$^{-1}$.

Jones has demonstrated that the benzyl cation could also be formed using dibenzylsulfide as a precursor. Recent attempts to obtain a formation rate constant were not successful. However, several interesting observations were made. Figure 16 shows spectra of a $2 \times 10^{-3}$ M solution of dibenzylsulfide irradiated by an 80 nsec electron pulse. The spectra were obtained at 300 nsecs after the pulse and at 5 μsecs after the pulse. The spectra are quite complicated, indicating the existence of at least three absorbing species. A difference spectrum taken from 320 to 440 nm indicates that the benzyl cation has been formed after the pulse. As the spectra indicate, the absorption due to the benzyl cation makes only a small contribution to the total absorption at 363 nm, the absorption maximum of the benzyl cation. Furthermore, the species absorbing at both longer wavelengths and at shorter wavelengths are decaying while the benzyl cation is forming. These facts have precluded the use of the simple data analysis described above. However, the data were of sufficiently
Figure 16. Transient optical absorption spectra resulting from irradiation of a $2 \times 10^{-3}$ M solution of dibenzylsulfide in 1,2-dichloroethane. Spectrum A was obtained at 300 nsec after the 80 nsec electron pulse. Spectrum B was obtained 5 μsec after the pulse.
good quality to indicate that the half-time of the formation after
the pulse, at 363 nm, was independent of the concentration of dibenzyl-
sulfide. This observation suggests that the rate limiting process in
the formation of benzyl cations from dibenzyldisulfide is the dissoci-
ation of the dibenzyldisulfide radical cation. If this were the case,
the formation of the benzyl cation would follow first order kinetics
and the half-time of formation would be independent of precursor con-
centration. The second criterion seems to have been met. The quality
of the data would not permit determination of the kinetic order.

It has been suggested that the species (PhCH$_2$)$_2$S$^+$ may absorb
below 350 nm.$^{42}$ However, the spectrum below 350 nm is fairly compli-
cated and a kinetic study of the transients absorbing in that region
has not been attempted.

**Biphenyl Radical Cation.** It is expected that the same electron
transfer process responsible for the dissociative ionization of the
carbonium ion precursors is also responsible for the formation of
aromatic radical cations in 1,2-dichloroethane. Arai et al.$^{11}$ esti-
mated that the formation rate constants for aromatic radical cations
in 1,1-DCE were greater than 1 x $10^{10}$ M$^{-1}$ sec$^{-1}$. A more sophisticated
estimate of the formation rate constants for the biphenyl and
p-terphenyl radical cations in DCE was made by Shank and Dorfman.$^{16}$
They suggested that the values were greater than 3 x $10^{10}$ M$^{-1}$ sec$^{-1}$
for biphenyl at 25°C and greater than 1 x $10^{10}$ M$^{-1}$ sec$^{-1}$ for terphenyl
at -31°C. Neither Arai nor Shank was able to observe any formation
after the electron pulse.
This investigation reports the observation of formation of the biphenyl radical cation in solutions of DCE after pulse irradiation. When a $1.3 \times 10^{-4}$ M solution of biphenyl is irradiated with 80 nsec pulses of electrons, the spectra shown in Figure 17 are obtained. They match the spectrum for the biphenyl cation reported by Arai et al.\textsuperscript{11} The increase in absorption at 690 nm was clearly due to the formation of the biphenyl radical cation.

The formation rate curve was similar to that obtained for solutions of bromodiphenylmethane. There was a fast increase in absorption during the pulse followed by a slow increase after the pulse, eventually reaching a plateau value. The slow formation curve was linearized by plotting $\ln(D_\infty - D_t)$ vs. time. Thus, it was first order.

Formation after the pulse was observed for biphenyl concentrations ranging from $1.3 \times 10^{-4}$ M to $6.6 \times 10^{-4}$ M. The first order formation constants were linear in the biphenyl concentration. A plot of the first order constants against concentration of biphenyl is shown in Figure 18. The bimolecular rate constant for the electron transfer from the solute was $1.4 \times 10^{10}$ M$^{-1}$ sec$^{-1}$ at 21°C. This value is roughly a factor of two less than the value estimated by Shank, and is probably a diffusion limited rate constant.

Terphenyl Radical Cation. Dichloroethane solutions containing $5 \times 10^{-5}$ M to $6.7 \times 10^{-4}$ M of p-terphenyl show an increase in absorption at 455 nm following irradiation by an 80 nsec pulse. Figure 19 shows the spectra of a solution containing $9.6 \times 10^{-5}$ M p-terphenyl at the end of the electron pulse and at 420 nsec after the pulse. The
Figure 17. Optical absorption spectra of the biphenyl radical cation formed in a $1.3 \times 10^{-4}$ M solution of biphenyl in 1,2-dichloroethane. Spectrum A was obtained at 330 nsec after an 80 nsec electron pulse. Spectrum B was formed 1.3 µsec after the pulse.
Figure 18. Plot of the pseudo first order rate constant for the formation of the biphenyl radical cation from biphenyl vs. the concentration of biphenyl.
Figure 19. Transient optical absorption resulting from irradiation of a $1 \times 10^{-4}$ M solution of p-terphenyl in 1,2-dichloroethane. Spectrum a was obtained at the end of an 80 nsec pulse. Spectrum b was obtained 420 nsec after the pulse.
transient species responsible for the increase in optical density is the terphenyl radical cation. These spectra agree with those previously reported for p-Ph$_3^+$. Oscillograms obtained for all concentrations greater than 5 x 10$^{-5}$ M appeared as those described for benzhydryl cation formation from bromodiphenylethane. The formation curve obtained with 5 x 10$^{-5}$ M p-terphenyl showed a small initial decay immediately after the pulse. The decay was followed by a large, slow increase in absorption. That portion of the curve immediately following the decay was not analyzed. The remainder of the curve was linearized by plotting ln(D$^\infty$ - D$_t$) against time. The slow formation following the pulse was first order at all concentrations. A graph demonstrating that the first order rate constants extracted from the oscilloscope traces were linear in the concentration of p-terphenyl is shown in Figure 20. The second order rate constant for formation of the p-terphenyl cation from p-terphenyl was found to be 1.45 x 10$^{10}$ M$^{-1}$ sec$^{-1}$ at 21°C. This value most likely represents the diffusion limited rate constant.

Table 1 is a compilation of the rate constants for the formation of various molecular cations in DCE. These rate constants do not indicate the stabilities or the reactivities of the resulting cations. Rather, they reflect the reactivities of the various precursor compounds toward electron transfer.

One might expect that the rate constants in Table 1 would correlate with the gas phase appearance potentials of the cations from their various precursors. These appearance potentials, listed in Table 1, have been estimated from the ionization potentials in Table 2.
Figure 20. Plot of the pseudo first order rate constant for the formation of the p-terphenyl radical cation from p-terphenyl against the concentration of p-terphenyl.
and the bond energies in Table 3. It was assumed that increasing phenyl substitution at the carbon atom decreased the C—X bond energy. Furthermore, it was assumed that a benzyl—mercury bond is weaker than an iso-propyl—mercury bond.

Only those rate constants below the diffusion limit may be compared with the corresponding appearance potentials. It is interesting to note, however, that the formation rates are diffusion limited for those reactions in which the appearance potential of the solute derived cation is less than 9.23 eV. The electron transfer reactions involving triphenylmethanol, trityl chloride, and benzhydrol as precursor seem to increase in rate as the appearance potential decreases. However, the limited amount of data is insufficient to establish whether or not a linear free energy relationship might exist between appearance potential and formation rate constant.

**TABLE 1**

FORMATION CONSTANTS OF ARYLCARBONIUM IONS FROM VARIOUS PRECURSOR COMPOUNDS IN 1,2-DCE AT 24°C.

<table>
<thead>
<tr>
<th>Cation Formed</th>
<th>Precursor Compound</th>
<th>Formation Constant (M⁻¹ sec⁻¹)</th>
<th>Appearance Potential (eV/molecule)</th>
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</thead>
<tbody>
<tr>
<td>Ph₃C⁺</td>
<td>Ph₃CBr</td>
<td>8.4 x 10⁹</td>
<td>&lt; 9.17</td>
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<tr>
<td>Ph₃C⁺</td>
<td>Ph₃COH</td>
<td>5.7 x 10⁸</td>
<td>&lt; 10.60</td>
</tr>
<tr>
<td>Ph₃C⁺</td>
<td>Ph₃CCl</td>
<td>4.0 x 10⁸</td>
<td>9.34</td>
</tr>
<tr>
<td>Ph₂OH⁺</td>
<td>Ph₂OBr</td>
<td>1.6 x 10⁻¹⁰</td>
<td>9.23</td>
</tr>
<tr>
<td>Ph₂OH⁺</td>
<td>Ph₂CHOH</td>
<td>4.0 x 10⁻⁷</td>
<td>&lt; 10.66</td>
</tr>
<tr>
<td>PhCH₂⁺</td>
<td>(PhCH₂)₂Hg</td>
<td>1.3 x 10⁻¹⁰</td>
<td>&lt; 9.23</td>
</tr>
<tr>
<td>p-Ph₃⁺</td>
<td>p-Ph₃</td>
<td>1.45 x 10⁻¹⁰</td>
<td>8.8</td>
</tr>
<tr>
<td>Ph₂⁺</td>
<td>p-Ph₂</td>
<td>1.4 x 10⁻¹⁰</td>
<td>9.0</td>
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TABLE 2
IONIZATION POTENTIALS OF AROMATIC RADICALS
AND AROMATIC MOLECULES

<table>
<thead>
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<th>Radical or Precursor</th>
<th>Ionization Potential</th>
<th>Reference</th>
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</thead>
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<tr>
<td>PhC*</td>
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</tr>
<tr>
<td>Ph₂CH•</td>
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<td>37</td>
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<td>37</td>
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<tr>
<td>p-Ph₃</td>
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</table>

TABLE 3
BOND ENERGIES FOR CARBONIUM ION PRECURSORS
AND RELATED COMPOUNDS

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Energy (eV/molecule)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₃C—Cl</td>
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</tr>
<tr>
<td>Ph₂CH—Cl</td>
<td>2.43</td>
<td>38</td>
</tr>
<tr>
<td>Ph₂CH—Br</td>
<td>1.91</td>
<td>38</td>
</tr>
<tr>
<td>PhCH₂—OH</td>
<td>3.34</td>
<td>44</td>
</tr>
<tr>
<td>iso-C₃H₇—iso-C₃H₇_g</td>
<td>1.47</td>
<td>45</td>
</tr>
</tbody>
</table>

Contribution of Non-Diffusive Processes to the Formation of Molecular Cations in 1,2-Dichloroethane

It has been suggested that many of the formation rate constants for the arylcarbonium ions and aromatic radical cations are at the diffusion controlled limit. These bimolecular rate constants were
obtained from that portion of the formation rate curve which follows the pulse. However, as mentioned previously, there was also a fast increase in optical density during the pulse for each of the experiments reported in the previous section. If the fast increase in absorption corresponds to the formation of the cations derived from the solute, then they are being formed at a rate exceeding that of the diffusive process.

The literature contains abundant references to non-diffusive processes being involved in the formation of cationic species as an indirect result of radiation. The migration of positive charge through the matrices of solid alkyl chlorides, branched paraffins, and carbon tetrachloride seems to be well established.\(^{13}\) Obviously, a diffusive process is not involved in this migration. Formation of aromatic radical cations in dilute solutions with butyl chlorides as solvents has been recently examined both in the solid phase and in the liquid phase at low temperatures.\(^{14}\) The authors concluded that both diffusive and non-diffusive processes could lead to the formation of the aromatic cations. Only the non-diffusive process was responsible for the formation in the solid phase. In the liquid solutions, they suggested that both processes were occurring. The growth in optical density following the electron pulse was attributed to cation formation by the diffusive process. The much faster growth in absorption during the pulse was attributed to cation formation by an ultra-fast, non-diffusive process.

The rates of formation of aromatic radical cations in liquid solutions with cyclohexane,\(^{46}\) acetone,\(^{47}\) or 1,2-dichloroethane\(^{16}\) as
solvent, have been estimated to exceed the diffusion limited rate.

It has been demonstrated in the preceding section that in DCE the formation of molecular cations following the pulse can always be accounted for in terms of a bimolecular, diffusive process. Therefore, any contribution of an unusually fast, non-diffusive process would have to occur during the pulse.

Knowledge of the relative amount of molecular cations formed during the pulse in essential to evaluate the extent of the contribution of non-diffusive processes to the formation of molecular cations. In this investigation, the formation and decay of these cations were followed by optical detection. Figure 21 shows the spectrum obtained upon pulse irradiation of a sample of pure DCE. Transients absorbing in the 300 nm to 550 nm spectral region are completely formed during the pulse. Clearly, the absorptions due to the solvent must be accounted for in order to evaluate the optical density of the molecular cations at the end of the pulse. The following paragraphs describe the techniques used to quantitatively define the solvent contribution at the end of the pulse, and, thus, to estimate the fraction of molecular cations formed by non-diffusive processes.

Figure 22 shows a plot of optical density against time, at 445 nm for a solution of $5 \times 10^{-5}$ M of p-terphenyl in dichloroethane. The figure also shows O.D. vs. time for pure DCE at the same wavelength and for the same duration of pulse. Since the data presented by these curves were obtained from consecutive pulses from the linac, they are expected to be the result of the same dose, within 6%.
Figure 21. Transient optical absorption spectra obtained by irradiating pure 1,2-dichloroethane with a 600 nsec electron pulse. Spectrum A was obtained at the end of the pulse, and spectrum B was obtained 1 μsec after the pulse.
Figure 22. Change in optical density at 455 nm with time following an 80 nsec electron pulse for pure 1,2-dichloroethane (A) and a $5 \times 10^{-5}$ M solution of p-terphenyl in 1,2-DCE (B).
The short interval of initial decay following the pulse was apparent only at $5 \times 10^{-5}$ M or less of p-terphenyl. Formation curves obtained from solutions with concentrations of p-terphenyl exceeding $5 \times 10^{-5}$ M exhibited only formation immediately following the pulse. It is suspected that the decay portion of the trace was due exclusively to the transients derived from DCE.

If it is assumed that the solvent absorptions at 455 nm are independent of p-terphenyl concentration, the difference between the two absorption curves in Figure 22 will be an exact formation rate curve for the p-terphenyl radical cation. That is, the absorption will be due to p-Ph$_3^+$ exclusively. The formation rate curve obtained as the difference is shown in Figure 23.

This curve was found to fit first order kinetics from the end of the pulse to the plateau region. A plot of $-\ln(D_\infty - D_t)$ against time was a straight line with a slope, $m$, of $1.03 \times 10^6$ sec$^{-1}$, an intercept, $b$, of 2.55, and a linear correlation coefficient of 0.999. The slope corresponds to a pseudo-first order rate constant of the formation process. $D_\infty$ was found to be 0.0822. The excellent fit of the formation curve obtained by difference to an actual first order curve generated by the values of $D_\infty$, and the extracted values of the slope and intercept is also shown in Figure 23. The line is the first order curve obtained by plotting $D_t$ vs. time, where $D_t = D_\infty - e^{-(mt + b)}$

The first order curve corresponding to the formation of p-Ph$_3^+$ in the absence of solvent absorption was extrapolated to the middle of the pulse to estimate the amount of formation during the pulse due to diffusive processes.
Figure 23. Plot of a first order formation rate curve. The solid circles were obtained by a point by point subtraction of the two curves in Figure 22.
This amount was added to the optical density at the end of the pulse due to pure solvent. The sum was then subtracted from the composite absorption at the end of the pulse to estimate the contribution of non-diffusive processes to the formation of p-Ph$_3^+$ during the pulse. The treatment is concisely outlined by the following equation:

$$D_{\text{composite}} - (D_{\text{DCE}} + D_{\text{Ph}_3^+, \text{diffusive}}) = D_{\text{Ph}_3^+: \text{nondiffusive}} \quad (23)$$

In the event that the absorption due to solvent at 455 nm does not change upon addition of p-terphenyl, only 17% of the absorption at the end of the pulse could be attributed to ultra-fast processes. Of the total amount of p-Ph$_3^+$ formed from $5 \times 10^{-5}$ M solutions of p-terphenyl, this is only 6%.

Estimating the amount of a transient formed during a pulse by extrapolation to the middle of the pulse is a reasonable approximation. However, a more precise method would be to solve the differential equations, resulting from the assumed mechanism, for the concentration of the transient at the end of the pulse. During the study of yield curves, described in a following section, an analytical expression was derived from the optical density of a solute cation at the end of the pulse.

The expression is Equation (66) on page 127. All the parameters in this equation can be experimentally determined, providing the dose absorbed by the system of interest is known. The equation could not be applied to the data described above, since precise dosimetry was not
obtained during that experiment.

The treatment described above assumed that there would be no change in behavior of the solvent species absorbing at 455 nm, upon addition of p-terphenyl. Alternatively, one may estimate any change in the decay of the solvent species upon the addition of a precursor of molecular cation. This was done by observing the effect of benzyl cation formation upon the solvent species' absorption at 455 nm.

Dibenzylmercury was chosen as precursor since the rate constant for the formation of the benzyl cation from this compound is very nearly equal to that for formation of p-Ph$_3^+$ from p-terphenyl. Furthermore, the spectrum resulting from the transients produced by dibenzylmercury have minimal absorptions at 455 nm. Providing that any change in the solvent transients' decay at 455 nm is due exclusively to benzyl cation formation, this experiment gives a valid estimate of the change in the solvent species' decay upon addition of p-terphenyl. The following assumption has been made implicitly: Upon addition of dibenzylmercury, any change in the decay of the solvent species at 455 nm that is not due to cation formation would occur to a similar extent if the same concentration of p-terphenyl were added.

To detect any changes in transient absorptions resulting from the solvent, both 363 nm, the absorption maximum of the benzyl cation, and 455 nm were monitored as increasing amounts of dibenzylmercury were added to pure DCE. The results are presented in Table 4.
TABLE 4
OPTICAL DENSITY IMMEDIATELY FOLLOWING AN 80nsec ELECTRON PULSE
FOR VARIOUS CONCENTRATIONS OF DIBENZYL MERCURY IN DCE

<table>
<thead>
<tr>
<th>Concentration of Dibenzylmercury</th>
<th>Optical Density 363 nm</th>
<th>Optical Density 455 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.021</td>
<td>.027</td>
</tr>
<tr>
<td>5.63 x 10^{-5}</td>
<td>.026</td>
<td>.028</td>
</tr>
<tr>
<td>1.07 x 10^{-4}</td>
<td>.030</td>
<td>.028</td>
</tr>
<tr>
<td>2.10 x 10^{-4}</td>
<td>.037</td>
<td>.027</td>
</tr>
</tbody>
</table>

Since the absorption at 455 nm, is independent of the concentration of added solute, it appears that carbonium ion formation has no effect on the solvent species absorbing at 455 nm. However, it is possible that any decrease in absorption due to the solvent transient is masked by a compensating increase in absorption due to spectral overlap of the benzyl cation. The time resolved spectra of the transients resulting from irradiation of a $1.5 \times 10^{-4}$ M solution of dibenzylmercury in DCE appear in Figure 24. An upper limit to the change in solvent absorption was obtained according to the following procedure: The ratio of the extinction coefficient of the benzyl cation at 363 nm to its extinction coefficient at 455 nm was taken as the ratio of absorbance at 363 nm to the absorbance at 455 nm for the $t = 1500$ nsec spectrum. This ratio is correct or overemphasizes the contribution of the benzyl cation to the absorption at 455 nm, since it was assumed that the solvent species was no longer absorbing at 1500 nanoseconds.
Figure 24. Transient optical absorption spectra obtained after an 80 nsec electron pulse for pure 1,2-dichloroethane (1) and a 1.5 x 10^{-4} M solution of dibenzylmercury in 1,2-DCE (2). Spectra a, b, and c were obtained at the end of the pulse, 200 nsec after the pulse, and 1.4 μsec after the pulse, respectively.
Next, it was assumed that for the dibenzylmercury solution, the absorption at 363 nm immediately following the pulse was due solely to the benzyl cation. From the ratio of extinction coefficients, determined in the previous step, the absorption at 455 nm due to the benzyl cation was estimated. The absorption due to the solvent transients was determined by difference. The decrease in the absorption of the solvent transient at the end of the pulse, caused by addition of dibenzylmercury, was found to be 17%.

If the same change in solvent absorption occurred at 455 nm in the solution containing $5 \times 10^{-5}$ M p-terphenyl, the maximum contribution of non-diffusive processes to the formation of $\text{p-Ph}_3^+$ may be estimated using Equation 23. As judged by the absorbance unaccounted for by the solvent species and the cations formed by a diffusive process, less than 26% of the total optical density at the end of the pulse in Figure 22 results from non-diffusive processes. This amounts to approximately 10% of the total amount of $\text{p-Ph}_3^+$ formed.

This estimate of the extent of the contribution of non-diffusive processes to molecular cation formation must be regarded as an upper limit. The concentration of dibenzylmercury was deliberately chosen to be a factor of three greater than the concentration of p-terphenyl used in the experiment to produce the formation curve in Figure 22. Additionally, the assumption that only the benzyl cation was absorbing at 363 nm at the end of the pulse (for the dibenzylmercury solution) clearly underestimates the contribution of the solvent species to the absorption at 455 nm.
The first treatment either correctly estimates within experimental error, or overestimates the optical density of the solvent species at the end of the pulse. The second treatment underestimates the solvent absorption. Providing that the estimate of the number of molecular cations formed during the pulse by diffusive processes is correct, non-diffusive processes are expected to have contributed between 17% and 28% to the total optical density observed at the end of the pulse for the curve in Figure 22.

The experiments described above suffered from the disadvantage that they only permitted indirect determination of the contribution of the solvent transients to the observed optical density. Hence, the formation of the solute cation by non-diffusive processes could only be estimated.

Later studies demonstrated that irradiation of pure 1,2-dichloroethane with 80 nsec pulses gives rise to no measurable transient absorption in the region of 940 nm to 980 nm. The terphenyl radical cation has an absorption maximum of 960 nm. Therefore, observing the formation of p-Ph$_3^+$ in dichloroethane solutions by monitoring its absorption at 960 nm would enable the direct evaluation of the contribution of non-diffusive processes to the formation of solute cations and, it is assumed, carbonium ions.

Figure 25 shows a formation rate curve for p-Ph$_3^+$ at 960 nm obtained by irradiating a 3.3 x 10$^{-5}$ molar solution of p-terphenyl in DCE with an 80 nsec electron pulse. The time scale was chosen to emphasize the formation during and immediately following the pulse. Only one formation process was involved after the pulse, since
Figure 25. Rate curve at 960 nm showing the formation of the p-terphenyl radical cation from p-terphenyl. The vertical expansion is 20 mv/division.
that portion of the curve followed first order kinetics. The first order constants obtained were linear in solute concentration, indicating the normal bimolecular diffusive process. It is quite clear from Figure 25 that there was no abrupt change in the formation rate upon the termination of the pulse, thus demonstrating that no fast formation process was occurring only during the pulse.

In conclusion, the formation rate curves for p-Ph$_3$$^+$ at 960 nm indicate that there is no detectable contribution to the formation of solute derived cations by an ultra-fast, non-diffusive process in 1,2-dichloroethane at room temperature. All formation can be accounted for by the normal bimolecular process.

**Effect of Solvent Absorption Upon Formation Kinetics and Apparent Yield**

The time zero spectra presented in Figure 24 indicate that the solvent absorption at the end of the pulse is essentially undiminished by the formation of a molecular cation, at least in the 435-525 nm region. Thus, optical densities determined at the end of a pulse contain a contribution from the solvent species which can be rather accurately determined. Correcting the composite absorbance for this contribution is simply achieved by subtracting from it the optical density obtained at the end of a pulse when pure solvent is irradiated.

It would also be desirable to correct the composite absorbance for the contribution resulting from the solvent at other times. However, an exact correction would be extremely difficult since it would require the determination of the rate laws for the decay of the solvent transients in the presence of each precursor. It does appear,
though, that any analytical correction of the formation rate curves can be avoided without seriously affecting the determination of reasonably accurate values of the formation rate constant.

For all formation curves, that portion of the curve immediately following the pulse was untreated. It was assumed that for the portion of the rate curve that was analyzed, the changes in optical density due to the solvent species were insignificant compared to the changes in optical density caused by formation of the molecular cation. Thus, the contribution of the solvent absorption was essentially ignored after a short time following the pulse. Any significant contribution of solvent decay to the formation kinetics was expected to be indicated by deviations from the pseudo first order formation rate law. Deviations were never observed.

An excellent indication of the magnitude of the effect of solvent contribution on the bimolecular formation rate constants is available. The rate constant obtained by monitoring the p-terphenyl cation at 960 nm was $1.88 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ at 22°C. It will be recalled that there is no absorption by the solvent transients at this wavelength. Therefore, this rate constant may be regarded as being obtained with an exact correction for the solvent absorption, in this case zero. Correcting the rate constant to 21°C by using the activation energy for a diffusive process in DCE, (Appendix B, and the following section), one obtains $1.85 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. The rate constant obtained by monitoring p-Ph$_2^+$ at 455 nm was $1.45 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ at 21°C. This rate constant was obtained by ignoring the contribution of the solvent absorption. Uncertainty in each rate
constant is about ± 10%. The constant determined at 960 nm is believed to be the more correct value.

The two determinations of the rate constant are within 12% of their average value. I have judged the deviation in the rate constants to be acceptable. Therefore, ignoring the contribution of the solvent absorption after a short time following the pulse seems to be acceptable in analyzing formation rate curves.

In the determination of a yield curve, the maximum optical density of the molecular cation is plotted against the concentration of its precursor. The typical shape of a yield curve is shown in Figure 26. In the plateau region of the curve, Region 3, the concentration of precursor compound is sufficiently high that the formation of the cation is effectively complete at the end of the pulse. Thus, correction for the solvent absorption was simply accomplished by subtracting the optical density at the end of the pulse resulting from the irradiation of pure solvent. Justification of this correction is provided by the experiments presented in the section regarding non-diffusive processes. This correction is necessary in order to calculate accurate yields from the plateau value of the optical density.

It is reasonable to expect that the decay of the solvent species' absorbance either remains the same or is accelerated by the addition of precursor. For the purpose of correcting the yield curve, it was assumed that the decay was unaltered. Any error caused by this assumption is negligible for the plateau region, as discussed above, and also for the region of the lowest concentrations of precursor, Region 1. In Region 1, the absorption maximum occurs at times in
Figure 26. Shape of a typical yield curve.
which the solvent absorption has decayed to negligible values. The correction is least accurate in that region of the yield curve where the slope is changing most quickly, Region 2. In this region, the maximum optical densities occur at times within about 300 nsec after the pulse.

**Temperature Dependence of the Formation Rate of the Benzhydryl Cation**

The temperature dependence of the rate of formation of the benzhydryl cation from bromodiphenylmethane was examined. The reaction was observed at six temperatures ranging from 24.3°C to -25.6°C, and at four concentrations of precursor ranging from $6.5 \times 10^{-5}$ M to $6 \times 10^{-4}$ M. Since the concentrations were better than three orders of magnitude lower than the solubility limit of bromodiphenylmethane in DCE at room temperature, it was assumed that the nominal concentrations were the actual concentrations.

The portion of the formation curve following the pulse obeyed a first order rate law at all concentrations and all temperatures. First order rate constants obtained at each temperature were linear in concentration of precursor, indicating that the rate limiting step for formation was a bimolecular process. Second order rate constants were obtained by plotting $k_{\text{obs}}$ against concentration of precursor.

A plot of the natural logarithms of the second order constants against the reciprocal of the absolute temperature is shown in Figure 27. The resulting straight line is significant in that it indicates that the mechanism did not change with temperature. The slope and the intercept of the straight line were determined by a linear least squares program.
Figure 27. Plot of $\ln(k)$ for the formation of the benzhydryl cation from bromodiphenylmethane in 1,2-dichloroethane against $1/T$. 
According to the Arrhenius equation, the logarithm of the rate constant is related to the reciprocal of absolute temperature by

\[ \ln k = -\frac{E_a}{RT} + \ln A \]  

Thus, the activation energy, \( E_a \), can be determined from the slope of the line in Figure 27. It has been found to be 2.6 kcal/mole. Calculation of the activation energy for a diffusion limited process in DCE predicts an activation energy of 2.7 kcal/mole. This calculation appears in Appendix B. The excellent agreement lends support to the suggestion that the rate of formation of the benzhydryl cation from its brominated precursor is diffusion limited.

The preexponential factor for the formation reaction has been determined to be \( 1 \times 10^{12} \) M\(^{-1}\) sec\(^{-1} \) from the intercept of the Arrhenius plot in Figure 27. This value is not abnormally high compared to the frequency factors for other reactions in solution.

Yield Curves

The simplified reaction scheme for the formation of aromatic radical cations and carbonium ions,

\[ \begin{align*}
e^- + S & \longrightarrow S^+ + 2e^- & t \leq p \\
S^+ + PX & \longrightarrow S + P^+ + X^- & t \geq 0 \\
S^+ + P & \longrightarrow S + P^+ & t \geq 0
\end{align*} \]

predicts that under conditions of excess concentration of precursor, a plot of \( \ln(D_\infty - D_t) \) vs. time will be a straight line for times after
the pulse. The slope of the line will be the pseudo first order rate constant, \( k_{25}(P) \) or \( k_{22}(PX) \). Straight lines were indeed obtained, and the second order constants, \( k_{22} \) or \( k_{25} \), that were eventually extracted from the data were presented in Table 1.

The acceptability of representing the kinetically significant steps of the formation mechanism by Reactions (21) and (22) or (25) must be considered with respect to the following observation: Formation of the cations derived from the solute was observed in that section of the yield curve labelled Region 1 in Figure 26. If the simplified mechanism outlined above was strictly correct, all \( S^+ \) would react to form \( P^+ \), providing the concentration of precursor exceeds the concentration of \( S^+ \). Although the concentration of precursor was typically one to two orders of magnitude greater than \( S^+ \) throughout most of Region 1, all the solvent cations were obviously not being scavenged by the precursor.

Alternatively, Reactions (21) and (22) predict that the yield would increase linearly with precursor concentration for concentrations below that corresponding to the total amount of \( S^+ \) formed. Above the concentration in which the number of precursor molecules in the cell equals the number of solvent cations produced, the yield should be constant. The shape of the predicted yield curve is shown in Figure 28. The yield curve predicted by the simple mechanism obviously disagrees with the experimentally determined yield curves. These observations suggest a competition for \( S^+ \). The nature of the possible competing reaction will be discussed.
Figure 28. Shape of the yield curve to be expected if there were no reactions competing for $S^f$. The concentration of precursor at "a" corresponds to the total amount of $S^f$ formed by irradiation.
Scavenging of the electron by the solvent produces chloride ions, as mentioned in the Introduction. The chloride ion may be considered to react with the solvent cations according to the reaction

$$S^+ + Cl^- \rightarrow S + Cl.$$ \hspace{1cm} (26a)

If the solvent cation is actually a carbonium ion, the result of fragmentation, the reaction may be

$$S^+ + Cl^- \rightarrow SCl$$ \hspace{1cm} (26b)

Realistically, the rate constants for Reactions (26) are expected to be $10^{11} \text{ M}^{-1} \text{ sec}^{-1}$ or lower. The maximum concentrations of free anions and free cations generated in the kinetic experiments were normally $2 \times 10^{-6} \text{ M}$ or less. Thus, the first half time for the second-order decay of $S^+$ by Reactions (26) typically would be 5 $\mu$sec or greater. The half times for the formation of the solute cations were always considerably shorter than this. Thus, it is unlikely that any kinetically significant reaction competing for $S^+$ is second order.

A parallel first order reaction could effectively compete with the precursor for $S^+$. The reaction could be an elimination or a rearrangement to form a species that does not exchange charge with the precursor. The competing first order reaction might also involve impurities, providing their concentrations were in excess of the concentration of $S^+$. This condition is not unlikely, since the
concentration of $S^+$ is micromolar. The sum of the first order reactions competing with precursor for $S^+$ will be represented by the reaction

$$S^+ \rightarrow \text{products}$$  \hspace{1cm} (27)

Therefore, the mechanism of formation of carbonium ions might be represented by the reactions

$$e^- + S \rightarrow S^+ + 2e^- \hspace{1cm} t \leq p \hspace{1cm} (21)$$
$$S^+ \rightarrow \text{products} \hspace{1cm} t \geq 0 \hspace{1cm} (27)$$
$$S^+ + PX \rightarrow S + P^+ + X \hspace{1cm} t \geq 0 \hspace{1cm} (22)$$

The reactions

$$S^+ + PX \rightarrow S + PX^+ \hspace{1cm} (28)$$
$$PX^+ \rightarrow P^+ + X \hspace{1cm} (29)$$

need not be considered, since the rate of formation of the cation, $P^+$, was found to depend on precursor concentration in all experiments.

The differential equations arising from the proposed mechanism are

$$\frac{d[S^+]}{dt} = k_{21} - k_{27}[S^+] - k_{22}[S^+][PX] \hspace{1cm} t \leq p \hspace{1cm} (30)$$
$$\frac{d[S^+]}{dt} = -(k_{27} + k_{22}[PX])[S^+] \hspace{1cm} t \geq 0 \hspace{1cm} (31)$$
$$\frac{d[P^+]}{dt} = k_{22}[PX][S^+] \hspace{1cm} t \geq 0 \hspace{1cm} (32)$$
The duration of the pulse is represented by \( p \). These equations are solved in Appendix C.

From Appendix C, the above mechanism predicts that for \( t \geq p \)

\[
[P^+]_\infty - [P^+]_t = \frac{k_{22}[P^+]k_{21}}{(k_{22}[P^+] + k_{27})^2} \left\{ e^{p(k_{22}[P^+] + k_{27})} - 1 \right\} e^{-t(k_{22}[P^+] + k_{27})}
\]  

Thus, plots of \( \ln([P^+]_\infty - [P^+]_t) \) vs. time are expected to be linear, as in the case of the simplified mechanism. The slopes of these plots are linear in the concentration of precursor, yielding \( k_{22} \) as the slope. Thus, the same value of the second order rate constant is obtained regardless of whether Reaction (27) is included in the mechanism.

By including Reaction (27) in the mechanism, it is shown in Appendix C that

\[
[P^+]_\infty = \frac{k_{22}[P^+]k_{21}p}{k_{22}[P^+] + k_{27}}
\]  

\([P^+]_\infty \) corresponds to the concentration of molecular cations formed for a given concentration of precursor. Thus, Equation 34 is an analytical expression for the yield curve derived from the proposed mechanism.

The second order rate constants, \( k_{22} \), are those presented in Table 1.

The concentration of precursor is known from the experiment. Values
of $k_{27}$ and the product, $k_{21}p$ can be estimated from the experimental yield curve. $k_{27}$ is roughly 0.7 times the reciprocal of the half-time for the formation of $P^+$ when the yield is half its "plateau" value. $k_{21}p$ is the concentration of carbonium ion when all the solvent cations are scavenged by solute. It is estimated from the apparent plateau values of the yield curve. Exact values of $k_{21}p$ and $k_{27}$ are determined by fitting a plot of $[P^+]_0$ vs. $[PX]$ to the experimental yield curve.

Figure 29 shows the yield curve for the benzhydryl cation from bromodiphenylmethane when an 80 nsec pulse was used. The points were experimentally determined and the curve was obtained by fitting Equation (34) to the data points. The rate constant for Reaction (27) was found to be $5.9 \times 10^6$ sec$^{-1}$ and the maximum number of solvent derived cations that were scavenged corresponds to a concentration of $1.54 \times 10^{-6}$ M. For the dose delivered in this experiment, this corresponds to a yield of 1.1 molecules/100 eV in DCE.

Figure 30 shows the yield curve for the p-terphenyl radical cation in DCE. Assuming that p-terphenyl scavenges the same amount of positive charge for a given dose, as bromodiphenylmethane does, the extinction coefficient of p-Ph$_3^+$ at 960 nm is estimated to be 22,800 M$^{-1}$ cm$^{-1}$. The rate constant for Reaction (27) was found to be $2.1 \times 10^6$ sec$^{-1}$.

The fit of Equation (34) to the experimental yield curve for the benzyl cation from dibenzylmercury is shown in Figure 31. Assuming a yield equal to that for the benzhydryl cation, $\epsilon_{363} = 14,500$ for the benzyl cation. To obtain the curve shown in Figure 31, $k_{27}$ assumed the value of $7 \times 10^6$ sec$^{-1}$. 
Figure 29. Relative yield of the benzhydryl cation as a function of concentration of bromodiphenylmethane in 1,2-DCE. The wavelength monitored was 445 nm. The solid circles are experimentally determined points. The curve was calculated as described in the text.
Figure 30. Relative yield of the p-terphenyl radical cation as a function of concentration of p-terphenyl in 1,2-DCE. The wavelength monitored was 960 nm. The solid circles are experimentally determined points. The curve was calculated as described in the text.
Figure 31. Relative yield of the benzyl cation as a function of concentration of dibenzylmercury in 1,2-DCE. The wavelength monitored was 363 nm. The solid circles are experimentally determined points. The curve was calculated as described in the text.
Figure 32 shows the yield curve for the trityl cation from triphenylmethyl bromide when 80 nsec electron pulses were used. Precise dosimetry was not performed; however, the dose has been found to be essentially constant, for a given width pulse, on a day to day basis. Therefore, the dose was assumed to be the average value of \(9.5 \times 10^{16}\) eV/cc of DCE. Using the reported extinction coefficient of the trityl cation at its absorption maximum, the yield is estimated to be 0.98 molecules/100 eV. This is essentially the same as the yield of the benzhydryl cation from bromodiphenylmethane. \(k_{27}\) was found to be \(5 \times 10^6\) sec\(^{-1}\).

Figure 33 shows the yield curve for the trityl cation from triphenylmethanol. 80 nsec pulses were used, delivering a dose of \(1.02 \times 10^{17}\) eV/cc of DCE. Equation (34) generated a curve that fit the data points with \(k_{21}p = 4.43 \times 10^{-7}\) M and \(k_{27} = 1.1 \times 10^7\) sec\(^{-1}\). Thus, the yield of the trityl cation from its carbinol precursor, as determined by extrapolation of the yield curve to infinitely high precursor concentration, has been determined to be 0.261 molecules/100 eV in 1,2-DCE. This value is only approximately a quarter of the value expected on the basis of the carbonium ion yields from triphenylmethyl bromide and bromodiphenylmethane.

If it is assumed that \(G_{Ph_3}^+\) is equal to unity for the carbinol precursor, the value of \(k_{21}p\) in Equation (34) would be fixed at \(1.7 \times 10^{-6}\) M for the dose delivered in this experiment. \(k_{22}^{[PX]}\) was experimentally determined. Thus, \(k_{27}\) would be the only parameter in Equation (34) that could be varied to fit the experimental points. Figure 34 demonstrates that a satisfactory fit cannot be obtained if \(G_{Ph_3}^+\) is
Figure 32. Relative yield of the trityl cation as a function of concentration of triphenylmethyl bromide in 1,2-DCE. The wavelength monitored was 439 nm. The solid circles are experimentally determined points. The curve was calculated as described in the text.
Figure 33. Relative yield of the trityl cation as a function of concentration of triphenylmethanol in 1,2-DCE. The wavelength monitored was 439 nm. The solid circles are experimentally determined points. The curve was calculated as described in the text.
Figure 34. Solid circles represent the experimentally determined relative yields of the trityl cation at various concentrations of triphenylmethanol. These are the same points as in Figure 33. The curves were calculated as described in the text. It was assumed that the total amount of $S^+$ scavenged at high precursor concentrations would equal the amount scavenged by trityl bromide or bromodiphenylmethane for the same dose. The circles could not be fit by varying the only unfixed parameter, $k$, in Equation (30).
assumed to be equal to unity.

Although a yield curve was not determined for the trityl cation from triphenylmethyl chloride, it was quite clear from the data obtained in the determination of the formation rate constant that this precursor also gives a yield of cation that is less than unity. Likewise, it was obvious from the study of the formation rate curves that the yields of the benzhydryl cation from the chlorinated precursor and the carbinol precursor were reduced from that of the brominated precursor.

These observations are similar to those of Capellos and Allen.22 In cyclohexane, triphenylmethyl chloride scavenges all the free cations to yield trityl cations. Triphenylmethanol, on the other hand, scavenges only about one half the free cations.

Evidently, selective scavenging of the positive charge centers in the solvent is occurring when several of the carbonium ion precursors are used as solutes. Competition kinetic experiments may provide further information about the nature of the formation processes.

Deuterium Isotope Effects on the Reactions of the Benzhydryl Cation with Alcohols

The reactions of the benzyl cation and the benzhydryl cation with various aliphatic alcohols have been previously investigated.40,50 The reactions were followed by monitoring the decay of the carbocations at their absorption maxima. Although no product analyses were performed, it was expected that the products of these reactions would be the ethers, P—O—R, which would result from the reaction51
$$\text{F}^- + \text{ROH} \rightarrow \text{PO(H)R}^+ \quad (35)$$

However, there is also evidence that arylcarbonium ions might abstract a hydride ion from the carbon atom to which the hydroxyl group is bonded.\textsuperscript{52}

This investigation reports an attempt to distinguish between these two alternative reaction paths by kinetic methods. If the rate determining step in the reaction of the carbonium ion with the methanol is a hydride abstraction, then one would expect to observe a kinetic isotope effect if deuterium atoms were substituted for the hydrogen atoms on the carbon. No such effect is expected if the rate limiting step is the formation of the protonated ether, Reaction (35).

The precursor of the benzhydryl cation was bromodiphenylmethane. Its concentration was always sufficiently high so that no formation of the carbonium ion occurred after the pulse. The alcohols used as reactants were CD\textsubscript{3}OD and CH\textsubscript{3}OD. The concentration of added alcohol was always such that the reaction of interest competed overwhelmingly with the natural decay process. In the presence of 1–6 x 10\textsuperscript{-3} M of added alcohol, the decay of the benzhydryl cation was first order. Plots of the first order rate constants against the concentration of alcohol are shown in Figure 35 for both CD\textsubscript{3}OD and CH\textsubscript{3}OD.

It is quite clear from Figure 35 that the reactivity of the benzhydryl cation toward methanol is unaffected by deuterium substitution at the carbon atom. On the basis of the experimental results of Bartlett and McCollum,\textsuperscript{52} an isotope effect of approximately a factor of two would be expected if the hydride abstraction were rate limiting. Thus,
Figure 35. Plot of the pseudo first order rate constants for the decay of the benzhydryl cation in the presence of CH$_3$OD (x) and CD$_3$OD (*) vs. concentration of alcohol.
the principal reaction of the benzhydryl cation with methanol is the formation of the protonated ether, Reaction (35).

The curvature in the plots in Figure 35 was also observed for the reactions of the benzyl cation with methanol and water and for the benzhydryl cation with methanol, ethanol, and the water. A similar phenomenon was also encountered by Szwarc in the case of protonation reactions of aromatic radical anions with various alcohols in dimethoxyethane.

A linearization of the data is possible based on the following interpretation. At sufficiently high concentrations, these alcohols and water exist not only as monomers, but also as higher aggregates. Using the approach suggested by Szwarc, it is assumed that the alcohols exist in only two forms that are kinetically significant in the concentration range studied, as monomers and as dimers. It is further assumed that the fraction of alcohol in the dimeric form is small, in the concentration range studied, so that the concentration of monomer can be approximated by the nominal concentration of added alcohol.

If

$$2\text{ROH} \Leftrightarrow (\text{ROH})_2$$

then

$$[(\text{ROH})_2] = K[\text{ROH}]^2$$

The decay of the carbonium ion can be described by the equations

$$\frac{-d[P^+]}{dt} = k_m[\text{ROH}][P^+] + k_d[(\text{ROH})_2][P^+]$$
Figure 36. Plot of the ratio of pseudo first order rate constant to concentration of alcohol for the decay of the benzhydryl cation vs. concentration of alcohol. Dashed line and x’s are for CH₃OD. Solid line and solid circles are for CD₃OD.
The observed first order rate constant, $k^\circ$, is clearly a non-linear function of alcohol concentration. A plot of the relationship between $k^\circ/\left[R_{OH}\right]$ and $\left[R_{OH}\right]$.

$$k^\circ/\left[R_{OH}\right] = k_m + k_dK\left[R_{OH}\right]$$

should linearize the data. The intercept would be the monomer rate constant, $k_m$, and the slope would be the product, $k_dK$, of the dimer rate constant and the equilibrium constant. Figure 36 demonstrates that this treatment does linearize the data presented in Figure 35. $k_m = 1.6 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ and $k_dK = 2.9 \times 10^9 \text{ M}^{-2} \text{ sec}^{-1}$ for CD$_3$OD.

$k_m = 1.7 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ and $k_dK = 3.1 \times 10^9 \text{ M}^{-2} \text{ sec}^{-1}$ for CH$_3$OD.

If $K < 1$, which it must be in view of the linearity of the plots in Figure 36, then the dimer is much more reactive than the monomer. This indicates that the transition state is stabilized with respect to the reactants by hydrogen bonding.

**Kinetic Studies of the Trityl Cation with Trialkylamines**

The kinetics of the reactions of the benzyl and the benzhydryl cations with triethylamine, tri-$n$-propylamine, and tri-$n$-butylamine were previously investigated. The reaction presumably results in the formation of a quaternary ammonium ion:

$$\text{F}^+ + \text{R}_3\text{N} \rightarrow \text{PR}_3\text{N}^+$$
These reactions obeyed a pseudo first order rate law under the experimental conditions. The pseudo first order rate constants were linear in the concentration of amine. Thus, the second order rate constants for the reactions of these two arylcarbonium ions with the alkylamines were obtained by plotting the observed rate constants against the concentrations of amine.

In order to obtain additional data concerning the influence of steric effects on rate, the reactions of the trityl cation with alkylamines were examined. The precursor of the trityl cation that was used for these experiments was triphenylmethanol. Trityl bromide gives a higher yield of the trityl cation than triphenylcarbinol does. However, trityl bromide was observed to react spontaneously with tripropylamine in cyclohexane while triphenylcarbinol did not react. Trityl bromide also reacted spontaneously with aniline in DCE while triphenylcarbinol did not. To ensure that no reactions were occurring with the amines before pulse irradiation, the less reactive precursor, triphenylcarbinol, was used. Consequently, the yields of the carbonium ion in these experiments were less than their optimum values.

Several complications were encountered in these experiments. Firstly, the amine concentrations necessary for the reactions to occur on a convenient time scale result in the amine competing successfully for the solvent cations. Thus, the yield of the trityl cation is reduced. Secondly, the successful competition of the amines for $S^+$ introduces the additional problem of spectral overlap of transients derived from the amines with the trityl absorption. This problem was more severe with triethylamine and tripropylamine than with tributylamine.
The effects of these two problems were minimized by keeping the concentration of triphenylmethanol at least a factor of ten greater than the concentration of amine. Thus, an upper limit to the amine concentration was established. The concentration of the trityl precursor was about $2 \times 10^{-2}$ M for reactions with triethylamine and tripropylamine. For the reaction with tributylamine, the concentration of triphenylmethanol was $1 \times 10^{-1}$ M.

The final complication is a result of the low rate constants for the reactions of the trityl cation with the three alkylamines. The experimental rate curves could not be treated by the methods used for the other reactions reported in this dissertation. The specific rate of the reverse reactions were not negligible with respect to the forward reaction. First order kinetics were not observed because in addition to the pseudo first order forward reaction and the first order reverse reaction, a mixed order decay of the trityl cation with the counterion, $\text{Cl}^-$, was also occurring.

The kinetically significant reactions occurring after the pulse, for the experimental conditions, were

$$\text{Ph}_3\text{C}^+ + \text{R}_3\text{N} \rightarrow (\text{Ph}_3\text{C})\text{R}_3\text{N}^+ \quad (43)$$
$$\text{Ph}_3\text{C}^+ + \text{Cl}^- \rightarrow \text{Ph}_3\text{CCl} \quad (44)$$
$$ (\text{Ph}_3\text{C})\text{R}_3\text{N}^+ \rightarrow \text{Ph}_3\text{C}^+ + \text{R}_3\text{N} \quad (45)$$

The differential rate expressions resulting from these reactions are
\[ -d[\text{Ph}_3C^+] / dt = \]
\[ k_{43}[\text{Ph}_3C^+][R_3N] + k_{44}[\text{Ph}_3C^+][\text{Cl}^-] - k_{45}[(\text{Ph}_3C)R_3N^+] \quad (46) \]

\[ -d[\text{Cl}^-] / dt = k_{44}[\text{Ph}_3C^+][\text{Cl}^-] \quad (47) \]

\[ -d[(\text{Ph}_3C)R_3N^+] / dt = k_{45}[(\text{Ph}_3C)R_3N^+] - k_{43}[\text{Ph}_3C^+][R_3N] \quad (48) \]

The rate constant of interest, \( k_{43} \), was derived by simulating the system described above on a Systron Donner, SD 40/80, analog computer. The values of \( k_{43}[R_3N] \) and \( k_{45} \) were chosen by trial and error until the best fit to the experimental decay curve was obtained. Figure 37 shows a decay curve for the trityl cation in the presence of tributylamine. The experimental curve, which is in terms of absorbed light intensities and time, was converted to optical density against time. The solid line in Figure 37 is the computer simulation of the decay.

The value of the rate constant, \( k_{44} \), was required for this treatment. Since a suitable source of \( \text{Cl}^- \) was not available to allow Reaction (44) to be studied under pseudo first order conditions, the rate constant was derived by analyzing the second order natural decay of the trityl cation in DCE. From a plot of \( 1/D_{439} \) vs. time, \( k_{44} \) was found to be \( 8 \times 10^{10} \, \text{M}^{-1} \, \text{sec}^{-1} \), based on the reported extinction coefficient of the trityl cation.\(^{49}\)

This value most probably represents the diffusion-controlled limiting rate constant. The rate constants\(^{50}\) obtained under pseudo
Figure 37. A rate curve for decay of trityl cation in reaction with tributylamine. The points are taken from the observed rate curve. The solid line is a computer simulation of the decay process.
Figure 38. Schematic of the analog computer program used to solve Equations (46), (47), and (48). The identifying numbers of the potentiometers correspond to the rate constants $k_{43-3}$, $k_{44}$, and $k_{45}$. 
first order conditions for reactions of the trityl cation with iodide ion and bromide ion are $3.6 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ and $5.6 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, respectively. The increase in rate constants with increasing size of reactants is expected for diffusion limited reactions.

A schematic of the analog computer program used to obtain $k_{43}$ appears in Figure 38. The pseudo first order rate constants, $k_{43}[R_3N]$, which were obtained by using this program are plotted against concentrations of amines in Figures 39 and 40. The bimolecular rate constants corresponding to the slopes of these plots are listed in Table 5. The uncertainty in the rate constants for the reactions with the benzyl cation and the benzhydryl cation are ±15 to ±20%. Uncertainty in the rate constants for the reactions with the trityl cation, involving smaller ranges of amine concentrations, are ±30 to ±40%.

| TABLE 5 | RATE CONSTANTS FOR REACTIONS OF ARYLCARBONIUM IONS WITH TERTIARY ALKYLAMINES IN DICHLORETHANE AT 24°C (UNITS, M$^{-1}$ s$^{-1}$) |
|-----------|-----------|-----------|-----------|
|          | $(\text{C}_2\text{H}_5)_3\text{N}$ | $(\text{C}_3\text{H}_7)_3\text{N}$ | $(\text{C}_4\text{H}_9)_3\text{N}$ |
| PhCH$_2^+$ | $2.0 \times 10^{9}$ | $1.4 \times 10^{9}$ | $1.0 \times 10^{9}$ |
| Ph$_2$CH$^+$ | $1.2 \times 10^{9}$ | $7.7 \times 10^{8}$ | $5.4 \times 10^{8}$ |
| Ph$_3$C$^+$ | $1.3 \times 10^{8}$ | $1.3 \times 10^{8}$ | $7 \times 10^{6}$ |

The rate constants in this table show a fairly smooth trend. As phenyl substitution increases, they decrease. The amount of decrease is a factor of 1.8 in going from benzyl cation to benzhydryl cation.
Figure 39. Plots of pseudo first order rate constants for the decay of the trityl cation in the presence of tri-n-propylamine (•) and triethylamine (x) vs. concentration of amine.
Figure 40. Plot of the pseudo first order rate constant for the decay of the trityl cation in the presence of tri-n-butylamine vs. concentration of amine.
The rate constants decrease by an additional factor of roughly an order of magnitude in going from the benzhydryl to the trityl cation. This trend is to be expected as a result of both steric effects and increased charge delocalization. Both of these factors together produce a rather small effect in the rate. The rate constants also decrease with increasing size of the alkyl group in the trialkylamines. It seems that the steric effect dominates the opposing electronic effect of electron release by the alkyl groups.
APPENDIX A

INTEGRATION OF RATE EQUATIONS FOR A SIMPLIFIED MECHANISM
FOR THE FORMATION OF CARBONIUM IONS IN DICHLOOROETHANE

If competing reactions are negligible, the formation of a carbonium ion may occur according to the reactions

\[ e^- + S \rightarrow S^+ + 2e^- \quad t \leq p \quad (21) \]

\[ S^+ + PX \rightarrow S + P^+ + X^- \quad t \geq 0 \quad (22) \]

The differential equations resulting from these reactions are

\[ \frac{d[S^+]}{dt} = k_{21} - k_{22}[S^+][PX] \quad t \leq p \quad (49) \]

\[ \frac{d[S^+]}{dt} = -k_{22}[S^+][PX] \quad t \geq p \quad (50) \]

\[ \frac{d[P^+]}{dt} = k_{22}[S^+][PX] \quad t \geq 0 \quad (51) \]

Under the experimental conditions, \([PX] = \text{constant}\).

Rearranging Equation (50) and integrating gives

\[ \int_{S^+}^{[S^+]_t} d[S^+]/[S^+] = -k_{22}[PX] \int_{p}^{t} dt \quad (52) \]
\[ [S^+]_t = [S^+]_p e^{-k_{22}[PX](t-p)} \]  \hspace{1cm} (53)

From Equations (51) and (53), for \( t \geq p \)

\[ \int_{t}^{[P^+]_\infty} d[P^+] = \int_{t}^{\infty} k_{22}[PX][S^+]_p e^{-k_{22}[PX](t-p)} \]  \hspace{1cm} (54)

\[ [P^+]_\infty - [P^+]_t = [S^+]_p e^{k_{22}[PX]} p e^{-k_{22}[PX]t} \]  \hspace{1cm} (55)

Thus, a plot of \(-\ln([P^+]_\infty - [P^+]_t)\) against \( t \) is predicted to be linear with a slope equal to \( k_{22}[PX] \).
APPENDIX B

CALCULATION OF THE RATE CONSTANT AND ACTIVATION ENERGY

FOR A DIFFUSION-CONTROLLED REACTION

The diffusion limited rate constant for a bimolecular reaction not involving two ions may be calculated using the equation:

$$k_{\text{diff}} = \frac{2RT}{3000 \eta(T)} \left( 2 + \frac{r_a}{r_b} + \frac{r_b}{r_a} \right)$$  \hspace{1cm} (56)

The viscosity of the solvent, \(\eta(T)\), is expressed in poise and \(R\) is \(8.31 \times 10^7\) erg/°K-mole. The reactants are assumed to be spheres with radii \(r_a\) and \(r_b\).

It is difficult to determine the radii of the dichloroethane radical cation and bromodiphenylmethane, since neither is spherical. The following approximate treatment was used. From the density of 1,2-DCE at 24 °C and its molecular weight, an "average" volume of one molecule may be calculated. If this volume were spherical in shape, then

$$r = \left[ \frac{(3/4)\pi V}{1/3} \right].$$

This treatment indicates that the radius of 1,2-DCE is 3.16 Å. It is assumed that the solvent radical cation occupies the same volume as the neutral molecule.

Bromodiphenylmethane is a solid at room temperature. However, chlorodiphenylmethane is a liquid at 24 °C and its density is known. Using the treatment described for DCE, the radius of a molecule of
Ph$_2$CHCl has been determined to be 4.13 Å. The bond radii and van der Waals' radii of Cl and Br differ by only about 10%. Furthermore, the halogen atom contributes only a small fraction to the total volume of these halogenated precursor compounds. Therefore, it is assumed that the radius of a bromodiphenylmethane molecule is also 4.13 Å.

Substituting the value of the viscosity,\textsuperscript{56} from the plot in Figure 41, and the estimated values of the molecular radii into Equation (56), $k_\text{diff}$ is calculated to be $9 \times 10^9$ M$^{-1}$ sec$^{-1}$. If the estimated ratios of the radii are in error by as much as a factor of two, the calculated rate constant changes only by about 15%.

The temperature dependence of the viscosities of many liquids is expressed by \textsuperscript{57}

$$\eta = A e^{\Delta E/RT} \tag{57}$$

Figure 41 shows that DCE behaves according to this equation. The slope of the line in Figure 41 is $\Delta E/R$. $\Delta E$ is 2.17 kcal/mole for 1,2-DCE.

Equation (56) may be simplified by representing the temperature independent terms as a single factor, $a$. Using the Arrhenius equation,

$$k_\text{diff} = \frac{aT}{\eta} = A e^{-E_a/RT} \tag{58}$$

Upon substituting Equation (57) into Equation (58) and solving for $E_a$, it is found that

$$E_a = RT + \Delta E \tag{59}$$
Figure 41. Plot of the natural logarithm of the viscosity (expressed in centipoise) of 1,2-dichloroethane vs. the reciprocal of the absolute temperature.
Near room temperature, the activation energy for a diffusive process in DCE is predicted to be 2.7 kcal/mole. This value is in good agreement with the experimentally determined value of 2.6 kcal/mole.
If competition for $S^+$ is included in the formation mechanism, the kinetically significant reactions occurring during the time of formation are

$$
e^- + S \rightleftharpoons S^+ + 2e^- \quad t \leq p \quad (21)$$

$$S^+ \rightarrow \text{products} \quad t \geq 0 \quad (27)$$

$$S^+ + PX \rightarrow S + P^+ + X^- \quad t \geq 0 \quad (22)$$

The differential equations arising from these reactions are

$$\frac{d[S^+]}{dt} = k_{21} - k_{27}[S^+] - k_{22}[S^+][PX] \quad t \leq p \quad (30)$$

$$\frac{d[S^+]}{dt} = - (k_{27} + k_{22}[PX])[S^+] \quad t \geq p \quad (31)$$

$$\frac{d[P^+]}{dt} = k_{22}[PX][S^+] \quad t \geq 0 \quad (32)$$

Since $[PX]$ is a constant under the experimental conditions, Equation (30) can be solved by separating variables and integrating from $t = 0$ to $t \leq p$. 

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For times after the pulse, \([S^+]\) is found by separating variables and integrating

\[
\int_0^{[S^+]_t} d[S^+] / [k_{21} - (k_{22}[PX] + k_{27})[S^+]] = \int_0^t dt
\]

(60)

\[
[S^+]_t \leq p = \frac{k_{21}}{k_{22}[PX] + k_{27}} (1 - e^{-(k_{22}[PX] + k_{27})t})
\]

(61)

Substituting for \([S^+]_p\) from Equation (61),

\[
[S^+]_t \geq p = [S^+]_p e^{-(k_{27} + k_{22}[PX])(t - p)}
\]

(63)

Substituting Equation (64) into Equation (32) and integrating from \(t \geq p\) to \(t = \infty\), one obtains
\[
\int_{-\infty}^{t} [P^+]_0 - [P^+]_t = k_{22}[PX] \frac{k_{21}}{k_{27} + k_{22}[PX]}
\]

\[
[P^+]_t \geq p
\]

\[
\left\{ e^{(k_{27} + k_{22}[PX])p} \right\} - 1 \int_{t \geq p}^{\infty} e^{-(k_{27} + k_{22}[PX])t} dt
\]

\[
[P^+]_\infty - [P^+]_t = k_{22}[PX] \frac{k_{21}}{(k_{27} + k_{22}[PX])^2}
\]

\[
\left\{ e^{(k_{27} + k_{22}[PX])p} \right\} - 1 \ e^{-(k_{27} + k_{22}[PX])t}
\]

Thus, plots of \(-\ln([P^+]_\infty - [P^+]_t)\) vs. \(t\) are expected to be linear, as for the case presented in Appendix A. The formation rate constants presented in Table 1 were the slopes obtained by plotting the slopes resulting from plots of \(-\ln([P^+]_\infty - [P^+]_t)\) vs. \(t\) against \([PX]\).

\([P^+]_\infty\) is found by changing the limits of integration in Equation (65) to \(t = p\) and \(t = \infty\). The result of integration is

\[
[P^+]_\infty - [P^+]_p = k_{22}[PX] \frac{k_{21}}{(k_{27} + k_{22}[PX])^2} \left\{ 1 - e^{-(k_{27} + k_{22}[PX])p} \right\}
\]

Substituting Equation (61) into Equation (32) and integrating from \(t = 0\) to \(t = p\), with \([P^+]_0 = 0\), one obtains

\[
[P^+]_p = k_{22}[PX] \frac{k_{21}}{k_{27} + k_{22}[PX]} \left\{ p + e^{-(k_{27} + k_{22}[PX])p} \frac{-1}{k_{27} + k_{22}[PX]} \right\}
\]
Adding Equations (67) and (68), one obtains

\[
[F^+]_{\infty} = \frac{k_{22}[PX]k_{21}P}{k_{22}[PX] + k_{27}}.
\]

Equation (34) was used to calculate the yield curves presented in a previous section.
LIST OF REFERENCES


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