

effects correspond to transition states in which the proton resides at the midpoint of its transfer, and the smaller effects correspond to very little or nearly complete transfer, according to the base strength of the acceptor relative to that of the donor. Sodium anthracene and sodium naphthalene are similar in base strength, well below perylene dianion; benzyl carbanion has a higher base strength than perylene dianion. The apparent extremum for these limited data, which, in essence, constitute only three points, is consistent with this interpretation, the assigned order of acidity having been based on the rate constants for proton abstraction.

Sodium ion pairing of the benzyl carbanion enhances its reactivity toward hydroxylic proton donors. Both enhancement and reduction of reactivity by ion pair formation and by conversion to tight ion pairs has been reported for a number of anions in diverse reactions. The effect we have observed may be compared with those reported. Enhanced reactivity has been found in the protonation of aromatic radical anions by water²⁹ and in the fluoradenyl carbanion initiated cleavage of ethylene oxide,³² among other reactions. A common feature of these two cases and the benzyl carbanion protonation seems to be that the reaction proceeds from an extensively delocalized anion reactant to a substantially localized negative charge on the product, since alkoxide or hydroxide is formed. Viewed in the context of transition state theory, we may expect some stabilization, by coulombic interaction between the sodium ion and the negative charge, of the transition state in which the charge is localized, to some degree, upon the oxygen atom from which the proton is transferred. This stabilization would act to lower the

(32) C. J. Chang, R. F. Kiesel, and T. E. Hogen-Esch, *J. Amer. Chem. Soc.*, **95**, 8446 (1973).

activation barrier relative to that of the free anion, if the extent of stabilization is less in the ground state than in the transition state.

Reduced reactivity upon ion pair formation is found in the electron transfer from aromatic radical anions to alkyl halides¹⁴ or to aromatic hydrocarbons³³ and in the proton transfer from triphenylmethane to polystyryl carbanion.^{12a} These reactions have in common a relatively greater degree of delocalization of negative charge in the transition state. Stabilization by coulombic interaction with sodium ion is thus expected to be far less in extent than with the former case.

Another likely cause of the greater activation barrier for reaction of the ion paired species is the relatively low affinity for positive ions shared by the neutral molecules of the second group of reactants. This property is important because these reactants must displace ether molecules from the primary solvation shell of sodium ion to form the transition state. Many studies² indicate that the THF present in the primary solvation shell of sodium ion is strongly coordinated, and displacement by these molecules of lower sodium ion affinity is thermodynamically unfavorable. Therefore, such a displacement will tend to increase the activation barrier for the ion pair but will not contribute to that for the free anion. These considerations have been discussed recently.³⁴

Acknowledgment. We are pleased to acknowledge the effective efforts of John Richter and Ed Ray in maintaining the linear accelerator and the electronic detection equipment.

(33) N. Hirota, R. Carraway, and W. Schook, *J. Amer. Chem. Soc.*, **90**, 3611 (1968); G. Rämme, M. Fisher, S. Claesson, and M. Szwarc, *Proc. Roy. Soc., Ser. A*, **327**, 476 (1972).

(34) J. F. Garst, "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, p 570.

Submicrosecond Formation and Observation of Reactive Carbonium Ions¹

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Abstract: The triphenylcarbonium ion, $(C_6H_5)_3C^+$, and the benzyl cation, $C_6H_5CH_2^+$, have been formed and studied in submicrosecond times in 1,2-dichloroethane solution at room temperature using the pulse radiolysis method. The optical absorption spectra of both species were determined. The benzyl cation, which has heretofore not been observed, has an absorption maximum at 363 nm very similar to that of the benzyl carbanion which has recently been reported from our laboratory. Absolute rate constants for the reactions of benzyl cation with methanol, ethanol, bromide ion and iodide ion have been determined at 24°. The values are 7.4×10^7 , 1.3×10^8 , 5.2×10^{10} and $4.9 \times 10^{10} M^{-1} sec^{-1}$, respectively. The reactivity with benzene was too low to permit determination of a rate constant value, but a rough upper limit was estimated. This technique of generating and studying reactive carbocations in solution is of general applicability.

Carbocations are important intermediates in such a broad variety of organic reactions in solution that an extensive literature²⁻⁶ on this subject alone has de-

(1) This work was supported by the U. S. Atomic Energy Commission under Contract No. AT (11-1)-1763 and also, in part, by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(2) G. A. Olah and P. v. R. Schleyer, "Carbonium Ions," Vol. I, Interscience, New York, N. Y., 1968.

veloped. Their existence has been well established,

(3) G. A. Olah and P. v. R. Schleyer, "Carbonium Ions," Vol. II, Interscience, New York, N. Y., 1968.

(4) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, pp 250-303, 412-610.

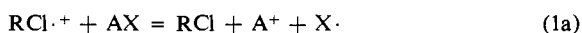
(5) J. F. Norris, *Amer. Chem. J.*, **25**, 117 (1901); J. F. Norris and W. W. Sanders, *ibid.*, **25**, 54 (1901).

(6) A. Báeyer and V. Villiger, *Chem. Ber.*, **35**, 1189 (1902); **35**, 3013 (1902).

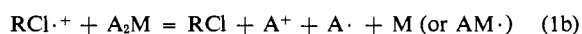
their properties⁷⁻⁹ documented (rather more fully for stable than for unstable varieties), and their role in reactions such as rearrangement, substitution, elimination, and others examined.¹⁰ Carbonium ions have generally been produced, for purposes of observation, in equilibrium systems involving solutions such as concentrated sulfuric acid, strong oxidizing agents in liquid sulfur dioxide, and the like. Accordingly, existing knowledge about their chemical reactivity has a relative basis. Little is known on an absolute basis about their reactivity in individual elementary reactions.

Formation of reactive carbonium ions by an impulse method, affording direct observation with submicrosecond time resolution, which we report in this paper, makes it possible to observe highly reactive carbonium ions, to determine their optical absorption spectra, and, more particularly, to evaluate absolute rate constants for many elementary reactions of these species. The fast reaction method we have used is the pulse radiolysis method. Carbonium ions may be formed in halocarbon solvents such as 1,2-dichloroethane by ionization and subsequent dissociation of appropriate solutes following irradiation of the solution by a pulse of high energy electrons.

This method of formation was conceived on the basis of our earlier work^{11,12} in which aromatic cation radicals were produced from aromatic compounds in halocarbon solvents by pulse radiolysis. Upon irradiation, the electrons resulting from the ionization become localized on a halide ion, while the solvent counterion, RCI^+ , remains free to exchange charge with solute molecules. *Nondissociative* ionization by charge exchange results in the formation of cation radicals. *Dissociative* ionization, using appropriate solutes, results in the formation of the carbocations



or



The method has been applied here to the formation of the triphenylcarbonium ion, $(\text{C}_6\text{H}_5)_3\text{C}^+$, the optical absorption spectrum of which is known, and to the formation of the benzyl cation, $\text{C}_6\text{H}_5\text{CH}_2^+$, which has, heretofore, not been observed. We have obtained the ultraviolet absorption spectrum of benzyl cation and have determined absolute rate constants for some elementary reactions of this ion.

Experimental Section

The source of the electron pulse in these fast reaction studies, as in our earlier work,¹¹⁻¹³ was a Varian V-7715A electron linear accelerator delivering 3-4 MeV electrons at a pulse current of about 300 mA for pulse duration of 100-1500 nsec and about 600 mA for

(7) N. C. Deno, P. J. Groves, and G. Saines, *J. Amer. Chem. Soc.*, **81**, 5790 (1959); G. A. Olah, C. U. Pittman, Jr., R. Waack, and M. Doran, *ibid.*, **88**, 2331 (1966).

(8) A. G. Davies and E. C. Baughan, *J. Chem. Soc., London*, 1711 (1961).

(9) G. Fraenkel, R. E. Carter, A. D. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5846 (1960); C. A. Cupus, M. B. Comisarow, and G. A. Olah, *ibid.*, **88**, 361 (1966).

(10) D. M. Brouwer and H. Hogeveen, "Progress in Physical Organic Chemistry," Vol. 9, A. Streitwieser, Jr., and R. W. Taft, Ed., Wiley-Interscience, New York, N. Y., 1972, pp 180-237.

(11) S. Arai, H. Ueda, R. F. Firestone, and L. M. Dorfman, *J. Chem. Phys.*, **50**, 1072 (1969).

(12) N. Shank and L. M. Dorfman, *J. Chem. Phys.*, **52**, 4441 (1970).

(13) W. D. Felix, B. L. Gall, and L. M. Dorfman, *J. Phys. Chem.*, **71**, 384 (1967).

pulse duration less than 80 nsec. Electron pulses ranging from 20 to 800 nsec were used in this work. All transient optical absorption spectra were determined using an R.C.A. 1P28 detector with an S-5 response. A Bausch and Lomb grating monochromator, type 33-86-25, $f/3.5$, with a dispersion factor of 7.4 nm/mm was used. Appropriate Corning filters were used to eliminate second-order components from the analyzing light beam.

Our standard reaction cells, equipped with high-purity silica windows and a cell length of 20.0 mm, were used in most runs with a double pass of the analyzing light beam. Accordingly, the optical path length was 40.0 mm. A full description of the optical arrangement and the electronic detection system has been provided elsewhere.¹³ All data reported herein were accumulated at room temperature.

The solvent used exclusively in this work was 1,2-dichloroethane (1,2-DCE) reagent grade from Matheson Cole and Bell. This was purified by washing with a portion of concentrated H_2SO_4 followed by several washes with distilled water. The solvent was then washed with a 10% sodium carbonate solution, washed several times with distilled water, and finally dried over barium oxide. It was then transferred to a storage bulb and degassed by repeated freezing-evacuation-thawing cycles. The desired quantity of solvent was then distilled *in vacuo* to the reaction cells just prior to the runs.

The following compounds were used as carbonium ion precursors: dibenzylmercury from Alfa Inorganics, dibenzyl sulfide from Eastman, methyl benzyl sulfide from K & K Laboratories, benzyl bromide from Chemical Samples Co., and triphenylmethyl chloride from J. T. Baker Chemical Co. The dibenzylmercury was recrystallized from ethanol. The methyl benzyl sulfide was doubly vacuum distilled after being thoroughly degassed. The benzyl bromide was washed with a 10% sodium carbonate solution followed by several washes with distilled water, dried over barium oxide, and doubly distilled *in vacuo* after being thoroughly degassed. The dibenzyl sulfide and triphenylmethyl chloride were used as obtained.

In addition the following substrates were also used either in observing scavenger effects or in the determination of absolute rate constants: aniline and benzene from J. T. Baker Chemical Co., methanol from Eastman, ethanol from U.S.I., tetraethylammonium bromide and tetraethylammonium iodide from ICN-K & K Laboratories. The aniline was purified by a double distillation performed *in vacuo*. Benzene was washed with concentrated H_2SO_4 , several portions of distilled water, a 10% sodium carbonate solution, and several portions of distilled water, in that order. It was then dried over barium oxide, distilled *in vacuo* to a freshly prepared sodium mirror, and finally distilled from the sodium mirror to a sample storage cell. Both the methanol and the ethanol were distilled *in vacuo* to bulbs containing freshly cut sodium. The resulting sodium alkoxide solutions were then degassed thoroughly and quantities of the respective alcohols distilled twice from their respective solutions to storage bulbs. The tetraethylammonium bromide and iodide were used as obtained.

Compounds having negligible vapor pressures were manually transferred in known quantities to the reaction cells just prior to each experiment. In cases where the compounds had an appreciable vapor pressure, the desired quantity was distilled into the reaction cell, *in vacuo*, from a small sample storage bulb and the amount determined by weight difference.

In order to determine the absolute rate constants for the reaction of benzyl cation with bromide ion and with iodide ion, it was necessary to determine the concentration of Br^- and of I^- , in short to determine the degree of dissociation of tetraethylammonium bromide and iodide in DCE. This was done conductimetrically. A conductivity cell capable of high vacuum operation was constructed with borosilicate glass and fitted with platinum ball electrodes in a manner similar to that described elsewhere.¹⁴ The bright platinum ball electrodes were platinized using a standard procedure.¹⁵ This conductivity cell was sealed to a sample preparation apparatus which allowed the independent preparation of two solutions, one with added salt and the other with no added salt. The device was constructed in such a way as to allow measurement of the specific conductivity of the pure solvent and subsequently to allow additions of known amounts of salt solution via a graduated pipet to the pure

(14) R. R. Dewald and J. H. Roberts, *J. Phys. Chem.*, **72**, 4224 (1968).

(15) L. Meites and H. C. Thomas, "Advanced Analytical Chemistry," McGraw-Hill, New York, N. Y., 1958.

solvent. The specific conductivity of the resultant solution was determined after each addition.

All manipulations were carried out under high vacuum conditions. Weighed amounts of salt were transferred to the salt solution reservoir. 1,2-Dichloroethane was distilled *in vacuo* to each reservoir and the volume for each determined by weight difference.

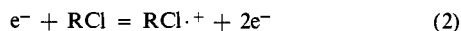
Determinations of specific conductance for these 1,2-dichloroethane solutions were carried out using an Industrial Instruments, Inc., type RC-18, conductivity bridge. The measurements were taken at $24 \pm 0.1^\circ$ using a thermostated water bath.

The cell constant was determined by measuring the resistance of an aqueous 0.1 M KCl solution at 25° and using the reported¹⁶ value of $0.012856 \text{ ohm}^{-1} \text{ cm}^{-1}$ to calculate the cell constant.

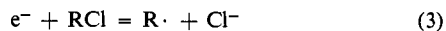
Results and Discussion

A. Optical Absorption Spectra. The anticipated mode of formation of carbonium ions from appropriate solute molecules by irradiation of solutions in dichloroethane is initiated, as indicated in reactions 1a or 1b, by charge transfer from the solute to the solvent cation. If the solute undergoes dissociative ionization, the carbonium ion will be formed.

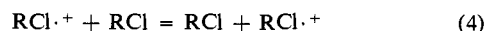
This mode of formation had been indicated in our earlier work^{11,12} on the formation of aromatic cation radicals from aromatic compounds for which the ionization by charge transfer is nondissociative. The principal events¹⁷ which occur are ionization (of the solvent almost exclusively) to produce secondary electrons



and localization of the electron on a halide ion as a result of dissociative attachment following energy degradation of the secondary electrons



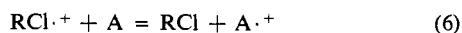
The positive charge center in the solvent will migrate, either by diffusion or by charge transfer



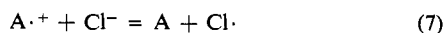
until either recombination with the chloride ion occurs



or charge is transferred from the solute.



In the earlier work,^{11,12} with solute molecules such as biphenyl, *p*-terphenyl, stilbene, and anthracene, the cation radicals, identified by their known optical absorption spectra,¹⁸ were formed by nondissociative ionization. The lifetime of the ion is then limited by recombination



Under our present nanosecond pulse conditions, the ions will have lifetimes of several microseconds or longer, sufficient to determine the optical absorption spectra as well as kinetic constants for reaction with various added solutes.

If now appropriate solutes are used which will undergo *dissociative* ionization, carbonium ions will be formed. We have used triphenylmethyl chloride to produce the triphenylcarbonium ion. We have used

(16) G. Jones and B. C. Bradshaw, *J. Amer. Chem. Soc.*, **55**, 1780 (1933).

(17) It should be pointed out that the ionization process (reaction 2) will involve both the incident high energy electrons and those secondary electrons in the degradation spectrum whose energy exceeds the ionization potential of RCl, whereas the attachment process (reaction 3) will involve thermal or near thermal electrons.

(18) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2375, 4372 (1966).

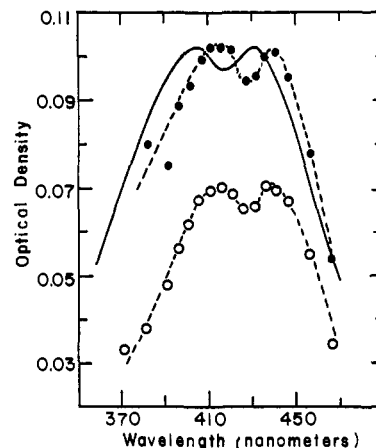


Figure 1. Optical absorption spectrum of the triphenylcarbonium ion in different solvents. The spectrum of this carbonium ion was obtained in a 1,2-DCE solution of $6.01 \times 10^{-3} \text{ M}$ triphenylmethyl chloride after an 800-nsec electron pulse (●) and at $3 \mu\text{sec}$ after the pulse (○). This spectrum is compared here with the spectrum of the triphenylcarbonium ion (—) obtained in 100% sulfuric acid (ref 18 and 19).

dibenzylmercury, dibenzyl sulfide, benzyl bromide, and methyl benzyl sulfide to produce the benzyl cation in 1,2-dichloroethane and to identify its optical absorption spectrum. Rate constants for some reactions of the benzyl cation have been determined.

Triphenylcarbonium Ion. The triphenylcarbonium ion was chosen to demonstrate the feasibility of the foregoing method of formation. This carbonium ion is well known¹⁹ and its optical absorption spectrum, which has been determined in equilibrium systems, is uniquely identifiable. Its formation has also been reported²⁰ in irradiated solutions of triphenylmethylcarbinol in cyclohexane.

The transient optical absorption spectrum formed following irradiation, by an 800-nsec pulse, of a degassed solution of triphenylmethyl chloride ($6.0 \times 10^{-3} \text{ M}$) in 1,2-DCE is shown in Figure 1. This spectrum, obtained at the end of the pulse, shows an absorption band with two peaks at 415 and 439 nm. The spectrum observed at $t = 3 \mu\text{sec}$ after the pulse shows an identical shape and location of the band maxima compared to the $t = 0$ spectrum, indicating that the entire spectrum is to be assigned to a single species. Under our conditions this transient absorption decays in accord with a second-order rate law with a first half-life of approximately $8 \mu\text{sec}$.

As may be seen from Figure 1, in which our observed spectrum is compared with the optical absorption spectrum of the triphenylcarbonium ion formed in a solution of triphenylmethanol in 100% sulfuric acid, it is clear that the transient species formed by pulse irradiation is the triphenylcarbonium ion. The spectra in the two systems are very nearly identical in shape with band maxima in 1,2-DCE showing a red shift of about 10 nm. This small spectral shift may very likely be due to solvent effects in such diverse solvent systems.

The reactivity exhibited by this transient absorption band toward bromide ion is consistent with the behavior to be expected of triphenylcarbonium ion. The

(19) (a) M. S. Newman and N. C. Deno, *J. Amer. Chem. Soc.*, **73**, 3644 (1951); (b) K. M. Harmon and A. B. Harmon, *ibid.*, **83**, 865 (1961).

(20) C. Capellos and A. O. Allen, *Science*, **160**, 302 (1968).

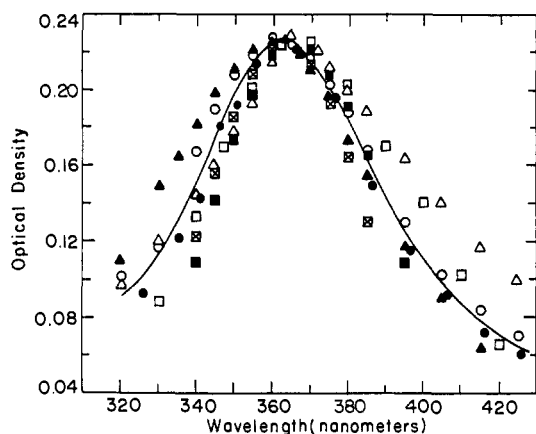


Figure 2. Optical absorption spectrum of the benzyl cation obtained by pulse radiolysis of various benzyl compounds in 1,2-DCE solution at room temperature: (●, ○) dibenzylmercury, the two sets of data representing different solutions and different conditions (the solid line is the curve which fits these dibenzylmercury data); (□, □, ■) dibenzyl sulfide, each set representing a different solution and different pulse length; (△) methyl benzyl sulfide; (▲) benzyl bromide. Each individual set of data has been normalized to the optical density at the absorption maximum.

transient reacts rapidly with bromide ion, as may be seen from the following experiment. In a solution of $6.6 \times 10^{-3} M$ triphenylmethyl chloride in 1,2-DCE to which $2.8 \times 10^{-4} M$ tetraethylammonium bromide had been added and irradiated with an 80-nsec pulse, the first half-life was reduced to 100 nsec from an observed half-life of $9 \mu\text{sec}$ in the absence of the bromide.

Benzyl Cation Spectrum. The benzyl cation is apparently a sufficiently reactive carbonium ion that it has not been possible to observe it in equilibrium systems. Consequently, the optical absorption spectrum of benzyl cation in solution is not known; nor, indeed, is there any information about its absolute reactivity. Because the optical absorption spectrum is not known, the identity of the transient band we believe to be that of benzyl cation (which we have generated in our pulse radiolysis experiments) must be assigned on the basis of systematic results involving different compounds. In short, what we demonstrate is the appearance of a common optical absorption band from sufficiently diverse precursor compounds that its identity as $\text{C}_6\text{H}_5\text{CH}_2^+$ is unequivocal. The compounds used which yield the common transient band through reactions 1a or 1b are: dibenzylmercury, dibenzyl sulfide, methyl benzyl sulfide, and benzyl bromide. The following are the experimental details.

a. Dibenzylmercury. The transient absorption band which we attribute to the benzyl cation, shown in Figure 2, was obtained at the end of a 400-nsec pulse in a 1,2-DCE solution $1.28 \times 10^{-3} M$ in dibenzylmercury. The shape of this transient band is not time dependent, as the spectrum taken at $4 \mu\text{sec}$ after the pulse, when considerable decay has taken place, shows the same band maximum and shape over the indicated wavelength region down to about 320 nm. This clearly indicates that the absorption band is to be attributed to a single transient species. These observations were duplicated in another experiment in which the spectrum was taken at the end of a 400-nsec pulse in a 1,2-DCE solution $9.3 \times 10^{-4} M$ in dibenzylmercury. As may be seen in Figure 2, in which the data are normalized to

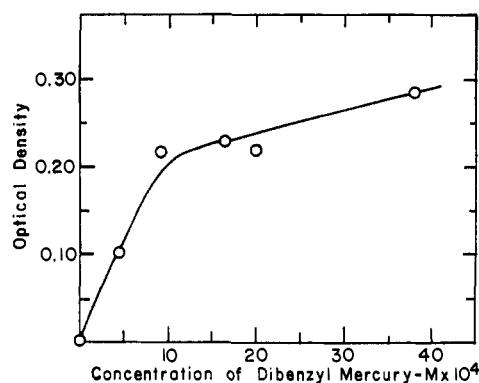


Figure 3. Yield (expressed in optical density) of the benzyl cation in 1,2-DCE as a function of dibenzylmercury concentration at a fixed pulse length.

the absorption maximum, the band shape is quite reproducible. The solid line is drawn through these two sets of data for dibenzylmercury. The first half-life for the decay of this species under our experimental conditions was about $1.6 \mu\text{sec}$.

The effect of scavengers upon the transient band centering at 363 nm is consistent with the behavior of a positively charged species. In the presence of 1 atm of air the spectrum remains unchanged and the lifetime of the transient is slightly increased. This observation is similar to the lack of any effect of oxygen upon radical cations^{11,12} in DCE but quite contrary to the behavior of radical anions²¹ which are effectively scavenged by oxygen. The transient reacts rapidly with aniline, with bromide ion, and with iodide ion as may be seen from the following results. The first half-life of the transient at 363 nm formed by irradiation, with a 400-nsec pulse, in a DCE solution $1.99 \times 10^{-3} M$ in dibenzylmercury, was reduced from about $1 \mu\text{sec}$ to about 300 nsec by the addition of $2.0 \times 10^{-3} M$ aniline. Bromide ion also reacts with this transient. The first half-life of the transient in a $4.8 \times 10^{-3} M$ dibenzylmercury solution in DCE irradiated with an 80-nsec pulse was reduced from about $2.4 \mu\text{sec}$ to 300 nsec by the addition of $6.8 \times 10^{-3} M$ tetraethylammonium bromide. Iodide ion has a similar effect. The first half-life of the transient produced by an 80-nsec pulse in a $3.5 \times 10^{-3} M$ dibenzylmercury solution was about $3 \mu\text{sec}$. This half-life was reduced to 700 nsec by making the solution $1.57 \times 10^{-3} M$ in tetraethylammonium iodide. Rate constants for the latter two reactions are evaluated in a subsequent section.

The yield of this transient, expressed in terms of optical density, was found to increase with dibenzylmercury concentration as may be seen in Figure 3. This dependence is very similar to that observed in the formation of radical cations in DCE and is indicative of the scavenging action of dibenzylmercury upon a reactive precursor in forming the 363-nm band.

A second, longer lived transient with a first half-life greater than $8 \mu\text{sec}$ was observed in the region below 320 nm. This transient was identified as the benzyl radical from its known absorption spectrum.²² A DCE solution $4.5 \times 10^{-4} M$ in dibenzylmercury, to permit trans-

(21) S. Arai and L. M. Dorfman, *J. Chem. Phys.*, **41**, 2190 (1964); N. Shank, Ph.D. Thesis, The Ohio State University, 1969.

(22) G. Porter and M. W. Windsor, *Nature (London)*, **180**, 187 (1957).

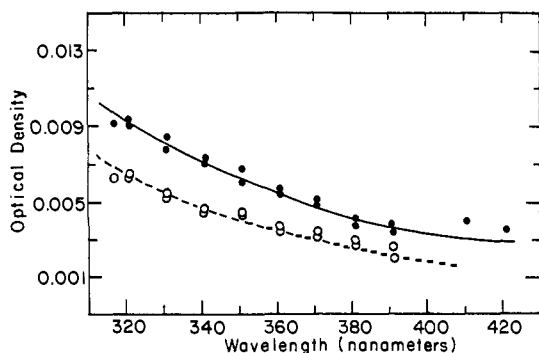


Figure 4. Optical absorption spectrum resulting after a 400-nsec pulse in pure 1,2-DCE: (●) points taken at the end of the pulse; (○) points taken at 1.54 μ sec after the pulse.

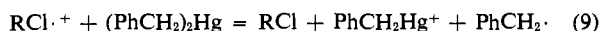
mission to shorter wavelengths, was irradiated with a 400-nsec pulse and the spectrum determined from 297 to 325 nm. The spectrum obtained at the end of the pulse, using a band pass of 1 nm to permit better spectral resolution, shows an absorption band with two narrow peaks at 306 and 317 nm, with the shorter wavelength peak having the lower intensity as in the benzyl spectrum,²² and with each showing a bandwidth of about 5 nm in accord with the published spectrum. The lifetime of the benzyl radical was not affected by bromide ion which did scavenge the 363-nm band.

It should be noted that any absorption due to species produced by irradiation of degassed 1,2-DCE itself is very weak and does not materially affect the other observed absorption bands. The spectrum obtained after a 400-nsec pulse in pure DCE is shown in Figure 4. The intensity of this absorption may be compared with that of the 363-nm band in Figure 2 since the optical path length used was the same. This weak absorption may very well be due to solvent radicals generated by irradiation.

The identity of the 363-nm band as the benzyl cation will be most definitively established from the systematic spectral results from all four compounds. Nevertheless, the fact that the benzyl radical is formed suggests that, in the formative charge transfer process, there are two possible reactions to be considered, namely



and



with the assumption that the two species are formed with comparable yields. Our data indicate this assumption to be at least semi-quantitatively true on the basis of our approximate results that $G_{(\text{C}_6\text{H}_5)_3\text{C}^+} \equiv G_{\text{RCI}} \cong 0.2$ molecule/100 eV based^{19b} on $\log \epsilon_{(\text{C}_6\text{H}_5)_3\text{C}^+} = 4.6$ and $G_{\text{PhCH}_2\cdot} \cong 0.2$ molecule/100 eV based²³ on $\epsilon_{\text{PhCH}_2\cdot} = 1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The systematic results will be seen to rule out PhCH_2Hg^+ .

b. Dibenzyl Sulfide. This compound is sufficiently different from dibenzylmercury so that the observation of a common band at 363 nm for the transient formed from this compound would identify the molecule fragment as benzyl cation. Other molecular fragments such as $\text{PhCH}_2\text{S}\cdot$ and PhCH_2S^+ , or the molecule ion $(\text{PhCH}_2)_2\text{S}^{\cdot+}$, would be distinct, spectrally, from their analogs obtained from the dibenzylmercury system.

(23) R. Hagemann and H. Schwarz, *J. Phys. Chem.*, **71**, 2694 (1967).

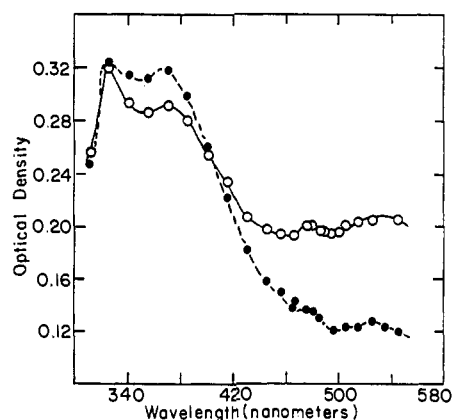


Figure 5. Optical absorption spectrum obtained after an 800-nsec pulse in a 1,2-DCE solution $6.37 \times 10^{-3} \text{ M}$ in dibenzyl sulfide. The spectrum is shown at time zero after the pulse (○) and at 1 μ sec after the pulse (●).

The transient spectrum obtained upon irradiation of dibenzyl sulfide in DCE reveals considerable complexity, being comprised of at least three transient species (exclusive of any derived from the solvent itself). Two of these appear to be involved in concurrent growth and decay, with the 363-nm band possibly having a longer wavelength transient as its precursor. The spectrum obtained after an 800-nsec pulse in a $6.37 \times 10^{-3} \text{ M}$ solution of dibenzyl sulfide in DCE is shown in Figure 5, where the spectrum is taken at $t = 0$ after the pulse and at $t = 1 \mu$ sec after the pulse. The band which is seen to grow in is the 363-nm band as may be established by taking the difference spectrum from the data in Figure 5 over the wavelength range 340 to 390 nm. This difference spectrum, from three different sets of data, is shown in Figure 2. Although this spectrum is obtained from a relatively small difference (5 to 15%) of two larger quantities, the three sets of data are in excellent accord and agree closely with the 363-nm band from dibenzylmercury. The transient species is thus very clearly the same as the one we have identified in the dibenzylmercury system. The complex dynamics of formation and decay are by no means fully understood and are to be a subject of further study. With a relatively short pulse length of 100 nsec neither the formation at 363 nm nor the decay at 480 or 540 nm fit a first-order rate law. Nevertheless, the time constant for both processes seems to be similar, a first half-life of about 2 μ sec having been found for both the formation and the decay. This suggests that the species absorbing beyond 460 nm may be either PhCH_2S^+ or $(\text{PhCH}_2)_2\text{S}^{\cdot+}$, possible precursors of benzyl cation.

Both the 363-nm band and the species beyond 460 nm are very reactive toward bromide ion as was shown by irradiating a DCE solution of dibenzyl sulfide containing $1.56 \times 10^{-4} \text{ M}$ tetraethylammonium bromide. The lifetime of the bands beyond 460 nm is reduced about threefold. The rate of decay of the 363-nm band is also sharply increased. Both bands are unaffected by the presence of air.

c. Methyl Benzyl Sulfide. This compound was selected not only because it is sufficiently different from dibenzylmercury and from dibenzyl sulfide but because the absorption bands from the possible molecular fragments resulting may be expected to lead to a considerably simpler composite spectrum from which the benzyl

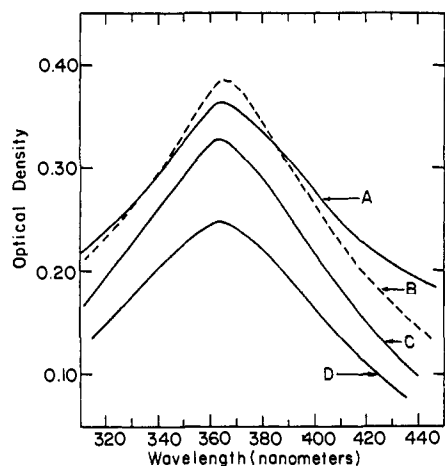


Figure 6. Optical absorption spectrum obtained after a 600-nsec pulse in a 1,2-DCE solution $3.41 \times 10^{-2} M$ in methyl benzyl sulfide. The spectrum is shown at time zero after the pulse (A), at $t = 800$ nsec after the pulse (B), at $t = 2.9 \mu\text{sec}$ after the pulse (C), and at $t = 7.1 \mu\text{sec}$ after the pulse (D).

cation band may be extracted more directly. This expectation is based on the certainty that any methyl fragment, whether charged or neutral, will not have an overlapping uv absorption at wavelengths longer than 300 nm. Furthermore, this lack of spectral overlap from 300 to 320 nm makes it easier to observe the benzyl radical if it is formed. The benzyl radical is not observed; its absence is consistent with dissociative ionization of the parent compound to form benzyl cation. The 363-nm band was observed directly in this system, without any substantial overlap from other absorbing species, as may be seen in Figure 6. This figure shows the spectrum obtained at times ranging from 0 to 7.0 μsec after a 600-nsec pulse in a $3.41 \times 10^{-2} M$ solution of methyl benzyl sulfide. The spectrum seems to consist almost entirely of a single species, which exhibits growing in as well as decay. The data show excellent reproducibility from one sample to another. The absorption maximum is again at about 363 nm, and the band shape, as may be seen in Figure 2, is identical with the band observed from the other compounds. We therefore identify this species as PhCH_2^+ . The species reacts efficiently with bromide ion and is not affected by the presence of oxygen.

d. Benzyl Bromide. A solution of this compound, upon irradiation, produces a complex spectrum which may be shown, from the time dependence, to consist of three separate species. The spectrum obtained after an 80-nsec pulse in a $7.58 \times 10^{-2} M$ solution of benzyl bromide in DCE is shown in Figure 7. The short-wavelength species, with a maximum at about 314 nm, has by far the longest lifetime. This band may be subtracted, with normalization at 314 nm, from the time zero spectrum, leaving a spectrum extending from 325 to 560 nm which consists of overlapping bands of the two shorter lived species. This latter composite difference of the two shorter lived species was defined more precisely from separate experiments with an 800-nsec pulse with resulting improved signal. The data in Figure 7 were used to define an absorption band with a maximum at 460 nm by subtracting the spectrum normalized to 314 nm at $t = 3.3 \mu\text{sec}$ from the spectrum at $t = 1.2 \mu\text{sec}$. If this 460-nm band, thus obtained, is

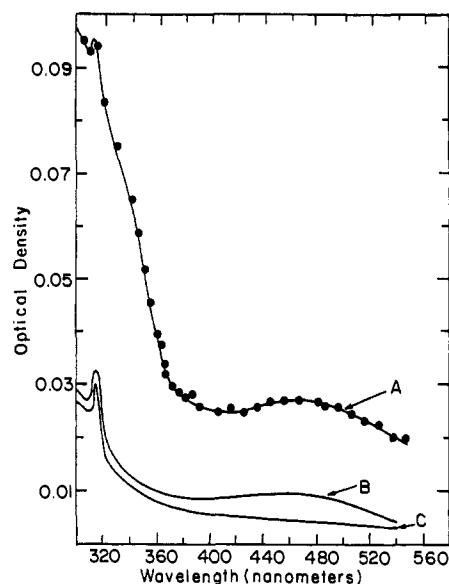


Figure 7. Optical absorption spectrum resulting from irradiation of a 1,2-DCE solution $7.58 \times 10^{-2} M$ in benzyl bromide. The spectrum is shown at time zero after an 80-nsec pulse (A), at $t = 1.2 \mu\text{sec}$ after the pulse (B), and at $t = 3.3 \mu\text{sec}$ after the pulse (C).

used together with the composite difference spectrum obtained from 800-nsec pulse irradiation to obtain a separation of the third and final band, this third band is found to have a maximum at 363 nm. This 363-nm band is shown in Figure 2 and may be seen to be identical with the 363-nm band obtained from the other three compounds.

The optical absorption band of benzyl cation in 1,2-DCE, which we have thus obtained, may be compared with the absorption band of the free benzyl carbanion in tetrahydrofuran which has recently been reported²⁴ from our laboratory. The benzyl cation in DCE has an absorption maximum at 363 nm and a width at half-height of the band of approximately 70 nm. The benzyl carbanion in THF has an absorption maximum at 362 nm and a width at half-height of approximately 95 nm. The absorption bands of the cation and anion are thus very nearly identical in band maxima, the carbanion absorption band being somewhat broader. The similarity of absorption spectra of cations and anions of conjugate hydrocarbons and of alternant hydrocarbons in particular may be expected on the basis of Hückel molecular orbital theory²⁵ and has indeed been found for radical anions and radical cations²⁶ as well as for carbonium ions and carbanions,²⁷ the latter formed by protonation of dinegative ions of aromatic hydrocarbons.

B. Absolute Reactivity. Absolute rate constants have been determined for the reaction of benzyl cation with methanol, ethanol, bromide ion, and iodide ion. The reactivity with benzene was so low that no rate constant could be determined; a rough value for the upper limit was estimated. In each case the absolute rate constant was determined by observing the decay of benzyl cation

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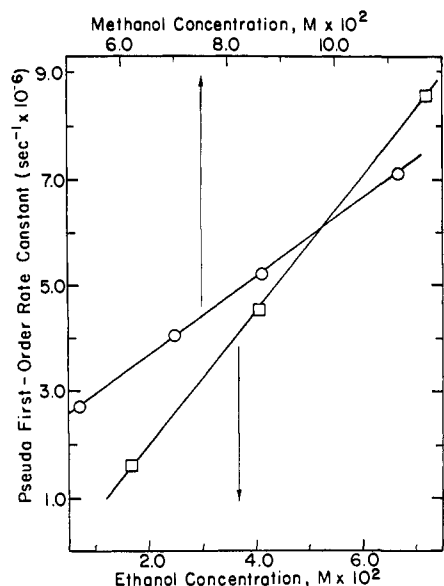


Figure 8. Plot of the pseudo-first-order rate constant for the reactions of benzyl cation with methanol and with ethanol in 1,2-DCE at 24° as a function of alcohol concentration. The abscissa for methanol is shown at the top of the figure and that for ethanol at the bottom. The rate constants are: methanol, $7.4 \times 10^7 M^{-1} \text{sec}^{-1}$; ethanol, $1.3 \times 10^8 M^{-1} \text{sec}^{-1}$.

at 363 nm, following an electron pulse of 20 to 80 nsec, in a solution containing known amounts of the reactant at concentrations such that the reaction in question competes overwhelmingly with the natural decay of benzyl cation. In the absence of any added reactant the benzyl cation decays in accord with a second-order rate law by combination with chloride ion.



This decay rate, in the absence of added reactant, was tested prior to the determinations for each individual system and was found to have a first half-time ranging from about 8 μsec to about 3 μsec for 20- to 80-nsec pulses, respectively. The reactive adduct was present in sufficient concentration (appropriate to the rate constant) to make the decay cleanly first order in all cases but benzene, with a half-life which ranged from about 400 to 30 nsec. From the slope of first-order plots ($\log D_t$ vs. time) the value of the pseudo-first-order rate constant was obtained. Subsequent plots of the pseudo-first-order rate constants vs. concentration yielded good straight lines, as will be seen, from which the absolute rate constant was obtained.

The rate constant for reaction with methanol was determined over a range of concentration of methanol from 0.05 to 0.11 M . A plot of k' (the pseudo-first-order constant) vs. concentration is shown in Figure 8. The absolute rate constant for reaction of PhCH_2^+ with methanol in DCE is $7.4 \pm 0.7 \times 10^7 M^{-1} \text{sec}^{-1}$ at 24°. Prior work⁴ has indicated that the product of this reaction is methyl benzyl ether. The rate constant for reaction with ethanol was determined over a range of concentration of ethanol from 1.6×10^{-2} to $7.2 \times 10^{-2} M$. A plot of k' vs. concentration is shown in Figure 8. The absolute rate constant for the reaction with ethanol in DCE is $1.3 \pm 0.2 \times 10^8 M^{-1} \text{sec}^{-1}$ at 24°. It is of interest to compare these rate constants with the rate constants for benzyl carbanion, recently reported²⁴ from this laboratory, in reaction with

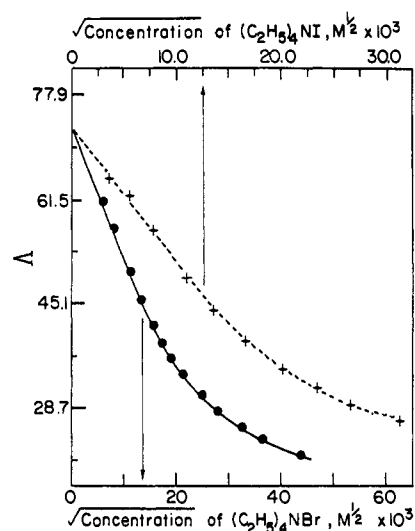


Figure 9. Plot of the equivalent conductance vs. the square root of the formal salt concentration for tetraethylammonium bromide and for tetraethylammonium iodide in 1,2-DCE at 24°. The abscissa for the bromide (●) is shown at the bottom and that for iodide (+) at the top. The values for Λ_0 are $73.4 \text{ ohm}^{-1} \text{cm}^{-1} M^{-1}$ for the bromide and $73.0 \text{ ohm}^{-1} \text{cm}^{-1} M^{-1}$ for the iodide.

methanol and ethanol. As may be expected, the order of reactivity, $k_{\text{ethanol}} > k_{\text{methanol}}$ for reaction with benzyl cation, is opposite to that for benzyl carbanion. The benzyl cation reaction with alcohol is a condensation reaction, while the benzyl carbanion reaction is a proton transfer reaction.

Rate constants have been determined for the reaction of PhCH_2^+ with bromide ion and with iodide ion from observed rate curves with added tetraethylammonium bromide and tetraethylammonium iodide over a concentration range of 1 to $10 \times 10^{-4} M$ and 0.5 to $5.6 \times 10^{-4} M$, respectively. In order to interpret these rate data, the dissociation constants for each salt in DCE were determined from conductivity measurements.

The conductivity data for both systems are shown in Figure 9 which presents a plot of the equivalent conductance Λ against the square root of the concentration of the salt. The value for Λ_0 , obtained from the intercept, is $73.4 \text{ ohm}^{-1} \text{cm}^{-1} M^{-1}$ for the bromide and $73.0 \text{ ohm}^{-1} \text{cm}^{-1} M^{-1}$ for the iodide. These values for the limiting equivalent conductance were used with the Ostwald dilution law^{28,29}

$$K_{\text{diss}} = \frac{\alpha^2 C}{1 - \alpha} = \frac{(\Lambda/\Lambda_0)^2 C}{1 - \Lambda/\Lambda_0} \quad (11)$$

where α , the degree of dissociation at any concentration, is given by Λ/Λ_0 and C is the concentration of the salt. As may be seen from the data in Table I, good constancy is obtained for K_{diss} , well within the experimental limits of our conductivity data, with values of 1.8×10^{-4} for the bromide and 1.8×10^{-4} for the iodide.

With these data, the rate constants for the reactions



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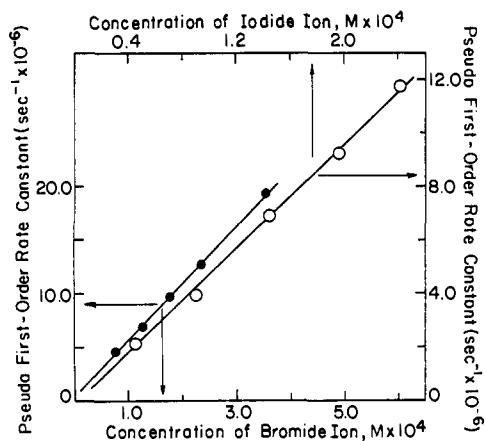


Figure 10. Plot of the pseudo-first-order rate constant for the reactions of benzyl cation with bromide ion and with iodide ion in 1,2-DCE at 24°C as a function of halide ion concentration. The abscissa and ordinate for bromide (●) are shown at the bottom and left side, respectively; the abscissa and ordinate for iodide (○) are shown at the top and right side, respectively. The rate constants are: $5.2 \times 10^{10} M^{-1} \text{sec}^{-1}$ for bromide and $4.9 \times 10^{10} M^{-1} \text{sec}^{-1}$ for iodide.

Table I. Dissociation Constants for Tetraethylammonium Bromide and Iodide in 1,2-DCE at 24°C

$[(C_2H_5)_4NBr],$ $M \times 10^4$	$K_{diss}, M \times 10^4$	$[(C_2H_5)_4NI],$ $M \times 10^5$	$K_{diss}, M \times 10^4$
0.653	1.77	6.18	1.73
1.244	1.81	11.83	1.69
1.776	1.79	18.60	1.72
2.421	1.82	27.73	1.73
2.934	1.76	40.41	1.75
3.583	1.79	55.15	1.81
4.499	1.80	71.01	1.81
6.220	1.89		
7.816	1.89		
Av	1.81 ± 0.08	Av	1.75 ± 0.06

were determined. A plot of k' vs. concentration of halide ion for these data is shown in Figure 10. The rate constants obtained are: $k_{12} = 5.2 \pm 0.6 \times 10^{10} M^{-1} \text{sec}^{-1}$ and $k_{13} = 4.9 \pm 0.5 \times 10^{10} M^{-1} \text{sec}^{-1}$ at 24°C. Since the values for Λ_0 are very nearly the same, it would appear from the rate constant values that the interaction radius is the same for bromide ion and

iodide ion. All the foregoing rate constants are shown in Table II.

Table II. Absolute Rate Constants for Reaction of Benzyl Cation in DCE at 24°C

Reactant	Rate constant, $M^{-1} \text{sec}^{-1}$
Benzene	Unreactive
Methanol	$7.4 \pm 0.7 \times 10^7$
Ethanol	$1.3 \pm 0.2 \times 10^8$
Bromide ion	$5.2 \pm 0.6 \times 10^{10}$
Iodide ion	$4.9 \pm 0.5 \times 10^{10}$

Attempts to determine a rate constant for reaction of benzyl cation with benzene proved to be unsuccessful by this method since the reactivity with benzene was found to be too low to permit observation of the reaction even at a benzene concentration of 0.7 M. With a 40-nsec pulse, the rate curves fit fairly closely to second order. The first half-time was 4.7 μsec at zero concentration of benzene, 4.2 μsec at 0.2 M benzene, and 4.1 μsec at 0.7 M benzene. These changes are not great enough, compared with our experimental uncertainty, to warrant any quantitative interpretation, and we can only conclude that benzene is unreactive. As a very crude estimate we would conclude that the rate constant for this reaction must be less than $10^4 M^{-1} \text{sec}^{-1}$.

Nomenclature. The question of appropriate and desirable nomenclature for carbocations is currently a subject of consideration in the literature^{30,31} and seems, to us, to be in a state of development. At this time, it seems inappropriate for us, with an interest largely in the kinetic behavior of these species, to enter into this discussion. Accordingly, we have used the nomenclature "carbonium ions," which will be familiar to most readers.

Acknowledgment. Discussions with colleagues here have been helpful in the course of this work, namely Professors Gideon Fraenkel and Paul Gassman. We are grateful to Mr. Ed Ray for maintaining the Linac and the detection equipment.

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