

Fast Reaction Studies of Carbanions and Carbocations in Solution

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Carbanions and carbocations play such a broad and pervasive role as reactive intermediates in organic reaction chemistry that an extensive and separate literature on the anionic¹⁻⁴ species and on the analogous cationic⁵⁻¹⁰ species has developed. Their existence is well established, and a good deal seems to be known about their structure.

Optical absorption spectra are known for a good many carbocations and for some carbanions. The carbocations for which the spectra are known are generally those which are stable in equilibrium systems and those which, like aryl-substituted carbocations, have their absorption bands in a conveniently accessible region of the spectrum.

Yet, there is a substantial paucity of information on the property of probably the greatest interest, namely the reactivity. Reactivity data have, for the most part, been obtained in a rather indirect manner. Rate constants are usually known on a relative rather than an absolute basis. The application of fast reaction methods to these species, with direct observation in real time, had been restricted to flow methods. The time resolution had thus been limited to milliseconds, inadequate for the study of the more reactive carbanions and carbocations.

Our recent application of the pulse radiolysis technique¹¹⁻¹⁴ to the study of the reactivity of carbanions^{15,16} and carbocations^{17,18} in solution has made it possible to form and observe these species on a submicrosecond time scale. Absolute rate constants have been determined for many of their elementary reactions. We have studied the benzyl carbanion,¹⁵ $C_6H_5CH_2^-$, free of cation pairing, as well as in its cation-paired state,¹⁶ $C_6H_5CH_2^-, M^+$, the commonly observed form. We have investigated a series of carbocations:^{17,18} the benzyl cation, $C_6H_5CH_2^+$, which had heretofore not been observed, as well as the benzhydryl cation, $(C_6H_5)_2CH^+$, and the trityl cation, $(CH_6H_5)_3C^+$.

This work on carbanions and carbocations follows from our recent investigations, by the pulse radiolysis method, of aromatic radical anions¹⁹⁻²¹ and radical

cations.^{22,23} With this radiation chemical technique, the solvated electron, in various liquids, serves as the reducing species to form the anionic intermediates by electron attachment to selected solutes. In other solvents, such as chlorinated hydrocarbons, the solvent cation serves as the oxidizing species to form the cationic intermediate by electron transfer from selected solutes. In the earlier work, the aromatic anion radicals and cation radicals were formed²¹ by electron attachment or by ionization, respectively, of solutes such as anthracene or biphenyl in a process which is nondissociative. The carbanions and carbocations, on the other hand, are formed by a *dissociative* electron attachment to or electron transfer from appropriate solutes.

Formation and Identification of Carbanions

The benzyl carbanion in its unpaired state, $PhCH_2^-$, as well as in its ion-paired state, $PhCH_2^-, Na^+$ (with alkali metal cations), has been formed and studied in solvents such as tetrahydrofuran. When a solution of a symmetrical metallorganic compound such as dibenzylmercury in tetrahydrofuran is irradiated, the solvated electron²⁴ formed in the tetrahydrofuran reacts with the solute in a dissociative attachment reaction:



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(15) B. Bockrath and L. M. Dorfman, *J. Am. Chem. Soc.*, **96**, 5708 (1974).

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(17) R. L. Jones and L. M. Dorfman, *J. Am. Chem. Soc.*, **96**, 5715 (1974).

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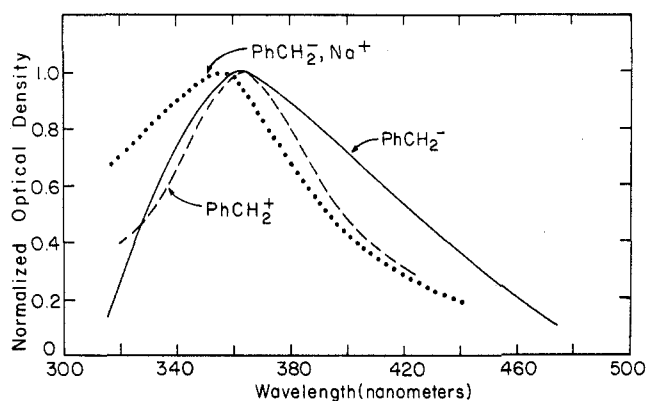
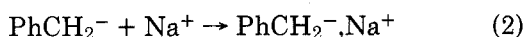


Figure 1. Optical absorption band of the benzyl carbanion, in the unpaired state, PhCH_2^- , and the sodium-paired state, $\text{PhCH}_2^-, \text{Na}^+$, both in tetrahydrofuran, and of the benzyl cation, PhCH_2^+ , in 1,2-dichloroethane solution. The optical density, normalized at the maximum, is plotted against wavelength.

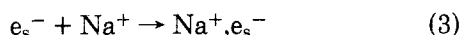
This reduction reaction is, in a sense, analogous to the reduction produced by dissolving an alkali metal in various liquids. The important differences are that, in the radiation experiment, no alkali metal need be present, and, secondly, the electrons may be introduced in a very short pulse. The benzyl carbanion, exhibiting a uv absorption band with a maximum at 362 nm, is formed. The benzyl radical is not formed, which is consistent with the stoichiometry of the reduction reaction (eq 1). The band at 362 nm, attributed to the benzyl carbanion, is slightly red-shifted from the band of $\text{PhCH}_2^-, \text{Na}^+$ in tetrahydrofuran, for which the maximum is reported²⁵ to be 355 nm.

The identification of the 362-nm band with the benzyl carbanion is further confirmed by allowing that species to react with sodium ion which has been added to the solution:

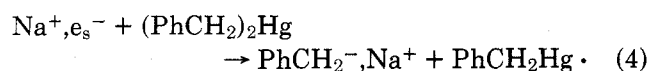


This reaction leads to the known, 355-nm band of the benzyl-sodium ion pair. The absorption band of each of these species is shown in Figure 1. The molar extinction coefficient of PhCH_2^- at the maximum is $8300 \text{ M}^{-1} \text{ cm}^{-1}$, based on the published²⁵ value of the extinction coefficient for $\text{PhCH}_2^-, \text{Na}^+$.

The species $\text{PhCH}_2^-, \text{Na}^+$ may also be formed in a different reaction sequence, again starting with the solvated electron. e_s^- may react first with sodium cation, to form the sodium-paired solvated electron²⁶ in tetrahydrofuran:



which then participates in a reduction analogous to reaction 1:



Whether the reaction proceeds by way of (1) and (2), or by (3) and (4), will depend on the ratio $[\text{Na}^+]/[(\text{PhCH}_2)_2\text{Hg}]$ in solution.

Since the species e_s^- , Na^+, e_s^- , PhCH_2^- , and $\text{PhCH}_2^-, \text{Na}^+$ each have characteristic absorption bands, their individual elementary reactions may be observed directly in real time following an electron

Table I
Absolute Rate Constants for Elementary Reactions in the Formation of PhCH_2^- and $(\text{PhCH}_2^-, \text{Na}^+)$ in Tetrahydrofuran at 24 °C

Reaction	k ($\text{M}^{-1} \text{ s}^{-1}$)
$e_s^- + (\text{PhCH}_2)_2\text{Hg}$	2.7×10^{10}
$e_s^- + \text{Na}^+$	7.9×10^{11}
$(\text{Na}^+, e_s^-) + (\text{PhCH}_2)_2\text{Hg}$	7.9×10^9
$\text{PhCH}_2^- + \text{Na}^+$	1.5×10^{11}

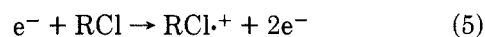
pulse. The absolute rate constants for each of reactions 1 to 4 have thus been determined^{15,16} and are given in Table I.

As is clear from the foregoing, the carbanion may be produced in the free state or the ion-paired state, as desired. Accordingly, the reactivity of either species may be determined. The solution, to be sure, also contains a counterion to the carbanion, namely the solvent cation, which is formed in the primary ionization of the solvent. Recombination of the carbanion with this counterion will be a lifetime-limiting process. However, the concentration of these ions produced under our conditions in the pulse radiolysis studies is generally lower than 10^{-5} M , so that the natural lifetime exceeds 1 μs . With a time resolution of 10 ns or better, this provides ample time for the study of reactions of the carbanions with a variety of added solutes.

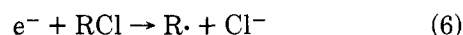
Formation and Identification of Carbocations

The benzyl cation, PhCH_2^+ , the benzhydryl cation, Ph_2CH^+ , and the trityl cation, Ph_3C^+ , were formed and investigated in halocarbon solvents. The latter two arylcarbenium ions were identified directly since their optical absorption spectra were known.²⁷⁻²⁹ The benzyl cation was identified not only from its analogous mode of formation but also from its formation from diverse compounds containing the benzyl group.

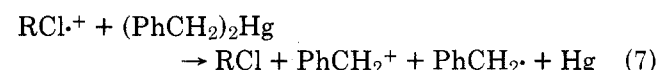
If a solution of dibenzylmercury in a halogenated hydrocarbon such as 1,2-dichloroethane is irradiated, the benzyl carbanion is not formed. The benzyl cation, PhCH_2^+ , is produced. This carbocation formation is believed to occur in the following way: The primary ionization of the solvent by the high-energy electrons and by the secondary electrons produces solvent cation radicals, and secondary electrons which thermalize.



In the halocarbon solvent, the secondary electrons, as they approach thermalization, undergo an attachment to the solvent, which is of course present at a high concentration. The attachment is likely dissociative, with the electron becoming localized on the chlorine:



This means that the electron is not available for attachment to dibenzylmercury, and, indeed, benzyl carbanion is not formed. The solvent cation radical, $\text{RCl}^{\cdot+}$, is, however, available, and depending on the ionization potential of the solute an electron-transfer reaction will occur, which, in the case of compounds such as dibenzylmercury, is dissociative:



(25) R. Asami, M. Levy, and M. Szwarc, *J. Chem. Soc.*, 361 (1962).

(26) B. Bockrath and L. M. Dorfman, *J. Phys. Chem.*, 77, 1002 (1973).

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The benzyl cation is formed, as is also the benzyl radical, which is identifiable from its spectrum.

Our data¹⁷ indicate that the yields of PhCH_2^+ and $\text{PhCH}_2\cdot$ are roughly the same, consistent with the stoichiometry of reaction 7. A series of systematic experiments with solutes other than dibenzylmercury, namely dibenzyl sulfide, methyl benzyl sulfide, and benzyl bromide, has been carried out. The result is that the same absorption band is formed in each case, indicating that benzyl cation is formed in a reaction analogous to (7). Preliminary determinations of the rate constants for the formation, by reactions analogous to (7), indicate that these range from $1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (for benzhydryl cation formation from bromodiphenylmethane) to $6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (for trityl cation formation from triphenylmethanol).

The benzyl cation exhibits a uv absorption band with a maximum at 363 nm. This band, as may be seen in Figure 1, is very nearly identical (smaller half-width, however) with the uv absorption band of the benzyl carbanion in THF. This similarity in the optical absorption band of the carbanion and carbocation is to be expected on the basis of molecular orbital theory.

What is the summation of the evidence identifying the 363-nm band in dichloroethane as the benzyl cation, which has not been observed before? To begin with, localization of the electron on the halide ion in dichloroethane solutions, as in reaction 6, and the role of the solvent cation as electron acceptor, as in reaction 7, had been indicated from our studies of aromatic cation radicals.^{22,23} Irradiation of dichloroethane solutions of aromatic compounds such as anthracene had resulted in the formation of the aromatic cation radical; the aromatic anion radical was not formed in halocarbon solvents.

Secondly, when analogous experiments were performed with dichloroethane solutions of bromodiphenylmethane or with triphenylmethyl chloride (or triphenylmethanol), the known spectra of the benzhydryl cation²⁷ or of the trityl cation,^{28,29} respectively, were observed, indicating the formation of these aryl-carbenium ions. The carbocation could be distinguished from the carbanion in the event the absorption spectra were similar, as with benzyl cation and benzyl anion, through the effect of selective scavengers such as oxygen. The carbanion in ether solutions is removed by oxygen since oxygen reacts effectively with the solvated electron as well as with the carbanion; the carbocation in dichloroethane was unaffected by oxygen in solution. Similarly, as expected, the carbocation was shown to be highly reactive toward halide ion, one of the types of electrophilic reaction we have investigated.

It was our expectation, then, that irradiation of dichloroethane solutions of dibenzylmercury would produce the benzyl cation. This was further substantiated by showing that a common absorption band (λ_{max} 363 nm) was formed in dichloroethane solutions, not only of dibenzylmercury but also of dibenzyl sulfide, methyl benzyl sulfide, and benzyl bromide. We have, of course, done no structure determination, but it is noteworthy that the tropylium ion, C_6H_7^+ , exhibits a substantially different optical absorption spectrum.

The arylcarbenium ions were formed with chloride ion as the counterion in solution. The combination reaction of these two ions was lifetime limiting. Since the

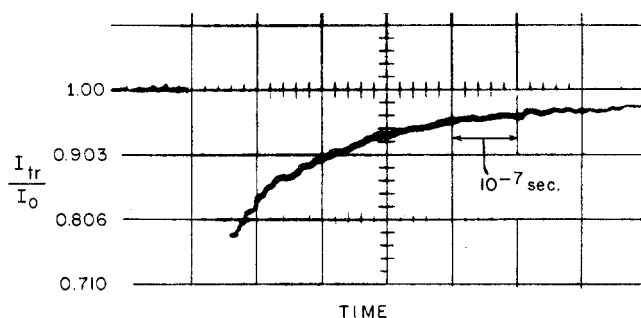


Figure 2. Typical rate curve, in this case showing the decay of the benzhydryl cation in 1,2-dichloroethane in reaction with tri-*n*-butylamine. The cation was formed following an 80-ns pulse.

lifetime, at the concentrations produced, was generally considerably longer than $1 \mu\text{s}$, it was quite feasible to determine the reactivity of the carbocations with various substrates, and rate constants for several types of electrophilic reactions were obtained.

Reactivity of Carbanions

Since the ions under investigation can be observed directly, in real time following an electron pulse, the absolute reactivity with added substrates may be determined in a fairly straightforward manner. This was done by monitoring the decay of the optical density, generally at the wavelength of the uv absorption band maximum. A typical rate curve is shown in Figure 2. The rate constants for the protonation of benzyl carbanion by various alcohols and by water in tetrahydrofuran solution were determined.



The differential rate expression for this elementary reaction is:

$$\frac{-d[\text{PhCH}_2^-]}{dt} = k_8[\text{PhCH}_2^-][\text{ROH}] \quad (9)$$

The rate law for the observed decay, under the condition $[\text{ROH}] \gg [\text{PhCH}_2^-]$, is first order. The pseudo-first-order rate constants were obtained from the slopes of the straight lines resulting from plots of log absorbance vs. time. These first-order constants were in turn plotted against the concentration of proton donor over a concentration range dictated by the rate constant and the time resolution (but always within 10^{-4} to 0.1 M). A straight line resulted in each case, from the slope of which the value of the particular constant, such as k_8 , was determined. Some typical examples are shown in Figure 3.

The benzyl carbanion could be formed and observed in either the unpaired state or in the ion-paired state, paired with cations such as sodium, lithium, or tetrabutylammonium by adding an appropriate dissociative salt. Accordingly, rate constants for the protonation of the carbanion in these various states were determined and are shown in Table II. The experimental uncertainty in the individual rate constants is approximately $\pm 15\%$.

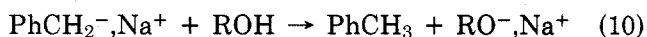
The data in Table II reveal, or are consistent with, a variety of physical phenomena such as: (a) the acid-base nature of the protonation reaction with which the trend may be rationalized, (b) the effect of cation pairing on the reactivity of the carbanion, and (c) the relative basicity of various hydrocarbon bases, by comparison with

Table II
Rate Constants for the Protonation of Free and of Ion-Paired Benzyl Carbanion in Tetrahydrofuran at 24 °C (Units, $M^{-1} s^{-1}$)

Carbanion	CH ₃ OH	C ₂ H ₅ OH	(CH ₃) ₂ COH	H ₂ O
PhCH ₂ ⁻	2.3×10^8	1.4×10^8	1.6×10^7	5.3×10^7
PhCH ₂ ⁻ ,Na ⁺	5.8×10^9	3.7×10^9	1.3×10^9	5.5×10^9
PhCH ₂ ⁻ ,Li ⁺	3.4×10^8		9.7×10^7	
PhCH ₂ ⁻ , N(C ₄ H ₉) ₄ ⁺	6.0×10^8		4.6×10^8	

data for other anions.¹⁵ To begin with, although the reactions may be considered to be "very fast", the rate constants are all below the diffusion-controlled limit. k_{diff} , estimated from the Smoluchowski equation, is about $1.4 \times 10^{10} M^{-1} s^{-1}$. Secondly, the trend in the value with the proton donor is readily understood in terms of the acid-base nature of the reaction. The value of k_8 increases with increasing acidity of the proton donor, as measured from the autoionization constants of the alcohol in either 2-propanol³⁰ or in dimethyl sulfoxide³¹ solution. To this may be added the observation of the deuterium isotope effect we have reported¹⁵ for the reaction of C₂H₅OD with PhCH₂⁻ and with PhCH₂⁻,Na⁺ for which $k_H/k_D = 1.2$ and 1.7, respectively. These effects, together with the dependency of k_8 upon alcohol acidity, imply the involvement of O-H bond breaking in the transition state for the reaction.

The effect of ion pairing upon the reactivity, not so readily predictable, is very marked for all three counterions investigated, which are all more reactive than the free ion. Indeed, the effect of ion pairing may dominate the effect of acidity of the proton donor. Sodium ion produces the greatest effects, with rate enhancement factors of 20 to 100. The counterion is, of course, participating in the reaction since it undergoes transfer from carbanion to alkoxide concurrent with the proton transfer.



Enhanced reactivity of ion pairs has also been found in reactions such as the protonation of aromatic radical anions by water³² and the fluoradenyl carbanion initiated cleavage of ethylene oxide.³³ It seems to be a common feature of all these cases that the reaction proceeds from an anion with extensively delocalized charge to an alkoxide or hydroxide on which the negative charge is substantially localized.

We infer that some stabilization may be expected by coulombic interaction between the sodium ion and the negative charge, the latter being localized to some degree, in the transition state, upon the oxygen atom from which the proton is transferred. Such stabilization would lower the 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.

Cation pairing, which has been shown to produce a substantial effect on the reactivity of the carbanion, also produces a small blue shift in the optical absorption

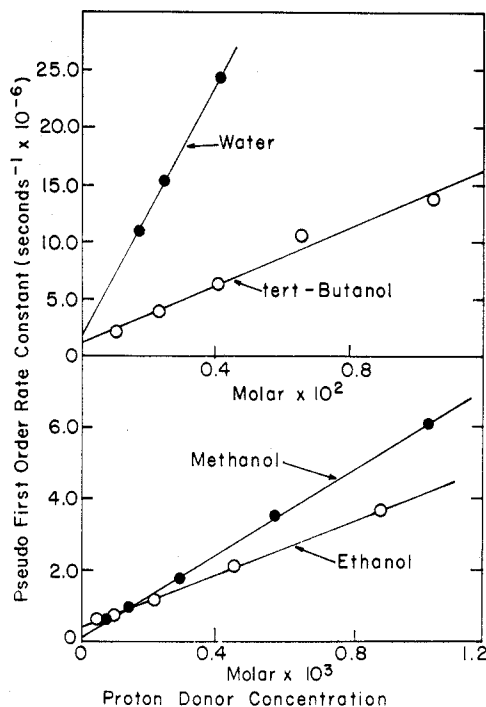


Figure 3. Pseudo-first-order rate constants for the decay of sodium-paired benzyl carbanion, PhCH₂⁻,Na⁺, in THF, plotted vs. concentration of proton donor with which the carbanion is reacting. The rate constants obtained from the slopes are given in Table II.

spectrum of the ionic species. The absorption maxima¹⁶ for PhCH₂⁻ in the unpaired state and for this carbanion paired with Na⁺, N(C₄H₉)₄⁺, and Li⁺, are 362, 355, 342, and 330 nm, respectively. The sodium has the smallest effect upon the absorption maximum; lithium ion has the largest. We have suggested¹⁶ that sodium, which has a large kinetic effect and a small optical effect, is a loose ion pair. Lithium shows a small rate enhancement and a larger optical effect. This may be related to the degree of polarity of the benzyl lithium ion pair. NMR studies³⁴ have shown that some degree of covalency exists for benzyl lithium. This partial covalent nature reduces the effective positive charge upon Li⁺, and hence its extent of enhancement of the proton transfer.

Finally, since our kinetic studies provide a measure of the basicity of carbon acids and thus complement a large body of knowledge³⁵ on the kinetic acidity of hydrocarbons, we have found it of interest to compare our rate constants¹⁵ with those obtained for other hydrocarbon bases by flow methods. For example, for the protonation reaction with methanol, the order of decreasing reactivity, comparing our data with perylene dianion³⁶ and with sodium anthracene,³⁷ is PhCH₂⁻,Na⁺ ($5.8 \times 10^9 M^{-1} s^{-1}$, tetrahydrofuran) > perylene²⁻,Na₂⁺ (1.2×10^6 , tetrahydrofuran) > anthracene⁻,Na⁺ (10.5, dimethylethane). These very large differences in reactivity may be interpreted in terms of the relative strengths of the conjugate acids of the hydrocarbon anions, toluene being the weakest and the dihydroanthracenyl radical the strongest acid. It is also interesting to note in the relevant literature^{15,36,37}

(30) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).

(31) C. D. Ritchie, "Solute-Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N.Y., 1969, p 230.

(32) S. Bank and B. Bockrath, *J. Am. Chem. Soc.*, **93**, 430 (1971); **94**, 6076 (1972).

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

(34) R. Waack, M. A. Doran, E. B. Baker, and G. A. Olah, *J. Am. Chem. Soc.*, **88**, 1272 (1966).

(35) J. R. Jones, "The Ionisation of Carbon Acids", Academic Press, London, 1973.

(36) G. Levin, C. Sutphen, and M. Szwarc, *J. Am. Chem. Soc.*, **94**, 2652 (1972).

(37) A. Rainis, R. Tung, and M. Szwarc, *J. Am. Chem. Soc.*, **95**, 659 (1973).

Table III
Rate Constants for the Reaction of Arylcarbenium
Ions with Halide Ions in Dichloroethane at 24 °C
(Units, $M^{-1} s^{-1} \times 10^{-10}$)

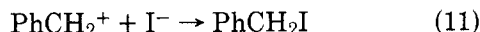
	I ⁻	Br ⁻	Cl ⁻
PhCH ₂ ⁺	4.9 ± 0.5	5.2 ± 0.6	
Ph ₂ CH ⁺	5.2 ± 0.6	7.0 ± 1.0	
Ph ₃ C ⁺	3.6 ± 0.5	5.6 ± 0.7	8.0 ± 2.5

that these three hydrocarbon bases (which include an anion, a dianion, and a radical anion) show very similar behavior, in terms of the relative rate constants, toward the same series of alcohol proton donors, even though the rate constants differ by 8 orders of magnitude.

Reactivity of Carbocations

The reactivities of the three carbocations which we have been able to form and to identify, namely the benzyl, benzhydryl, and trityl cations, were determined for a variety of electrophilic reactions by methods similar to those used for the carbanions. The nucleophiles for whose reactions absolute rate constants were determined are: halide ions, trialkylamines, and aliphatic alcohols.

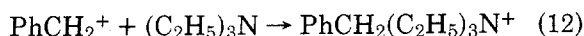
The rate constants for reaction of the carbenium ions with halide ions, such as iodide ion:



were determined in a solution containing an appropriate concentration of the dissociative tetraethylammonium halide salt. Halide ion concentrations were calculated from the ion dissociation constants in dichloroethane, which we had determined from conductivity measurements.¹⁷ The rate constants are given in Table III.

The rate constant for the reaction of trityl cation with chloride ion, which has a substantially larger uncertainty than the other rate constants in the table, was obtained in a different manner. This was obtained in a solution containing no added halide ion, so that the reaction in question represented the combination of the trityl cation with the chloride counterion. The rate curve was found to fit a second-order rate law, from which the rate constant could be determined only with the knowledge of the magnitude of the molar extinction coefficient³⁸ of trityl cation. This accounts for the larger uncertainty. These values, which are very nearly the same for the three arylcarbenium ions, seem to show a small trend with halide ion. The values likely represent the diffusion-controlled limiting rate constants for the ion combination reactions in question. The small increase is in the direction of increasing mobility of the anion, which in turn has an inverse dependence upon the ionic radius. The radius factor is, however, partly canceled in the Smoluchowski equation since it appears in both the interaction cross section and in the diffusion coefficient.

The reactivity of the three arylcarbenium ions with three tertiary alkylamines (triethyl-, tri-*n*-propyl-, and tri-*n*-butylamine) was also determined in order to examine the magnitude of the steric effects in these electrophilic reactions. The reaction presumably results in the formation of a quaternary ammonium ion:



(38) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).

Table IV
Rate Constants for Reactions of Arylcarbenium
Ions with Tertiary Alkyl Amines in Dichloroethane
at 24 °C (Units, $M^{-1} s^{-1}$)

	(C ₂ H ₅) ₃ N	(C ₃ H ₇) ₃ N	(C ₄ H ₉) ₃ N
PhCH ₂ ⁺	2.0 × 10 ⁹	1.4 × 10 ⁹	1.0 × 10 ⁹
Ph ₂ CH ⁺	1.2 × 10 ⁹	7.7 × 10 ⁸	5.4 × 10 ⁸
Ph ₃ C ⁺	1.3 × 10 ⁸	1.3 × 10 ⁸	7 × 10 ⁶

The rate constants obtained¹⁸ are given in Table IV. The uncertainty in all the rate constants except that for trityl cation is approximately ±15 to ±20%. In the cases for which the value was obtained¹⁸ from curve-fitting procedures, the uncertainty range was ±30 to ±40%.

The rate constants in Table IV, which are all below the diffusion-controlled limit, decrease in magnitude with increasing phenyl substitution of the carbenium ion. The decrease amounts to a factor of 1.8 in going from phenylcarbenium ion to diphenylcarbenium ion, and closer to an order of magnitude, and more, in going from diphenylcarbenium to triphenylcarbenium ion. The direction of the effect may be anticipated on the basis of the steric effect of increasing molecular complexity together with the electronic effect (increased charge delocalization with increased degree of phenyl substitution). It is, however, interesting that both factors together produce as small an effect as is observed. The rate constants also decrease, but to a lesser extent, with increase in the size of the alkyl group in the amines. It would seem, therefore, that the steric effect is dominant over the electronic effect of electron donation by the alkyl group which would produce an increasing trend.

The reactivity of two of these arylcarbenium ions with the aliphatic alcohols has been determined. It shows an interesting effect. We have concluded,¹⁸ from the observations which follow, that the reactivity with alcohol dimer in dichloroethane solution is higher than with monomer. It has been shown³⁹ that a product of the reaction of arylcarbenium ions with an aliphatic alcohol is the ether resulting from the condensation:



Apparently the ionic intermediate undergoes a deprotonation to form the ether. Evidence also exists,⁴⁰ in the case of trityl cation, for the occurrence of a hydride ion transfer. It should be made clear that we have performed no product analyses and are observing only the disappearance of the arylcarbenium ion. Observation of the rate curve for the reaction by monitoring the decay of the carbenium ion (benzhydryl cation in the case of reaction 13) shows that these rate curves follow a first-order rate law. However, the plot of the pseudo-first-order rate constant against alcohol concentration was found¹⁸ to deviate significantly from linearity, as may be seen in Figure 4. The slope of the curve increases with increasing alcohol concentration.

This may be rationalized on the basis of the following interpretation which leads to a linearization of the data. There is a good deal of independent evidence^{41,42} that alcohols in solution at sufficiently high concentration

(39) Reference 6, p 273.

(40) P. D. Bartlett and J. D. McCollum, *J. Am. Chem. Soc.*, **78**, 1441 (1956).

(41) G. Pimentel and A. L. McClellan, "The Hydrogen Bond", W. H. Freeman, San Francisco, Calif., 1960.

(42) N. D. Coggeshall and E. L. Saier, *J. Am. Chem. Soc.*, **73**, 5414 (1951).

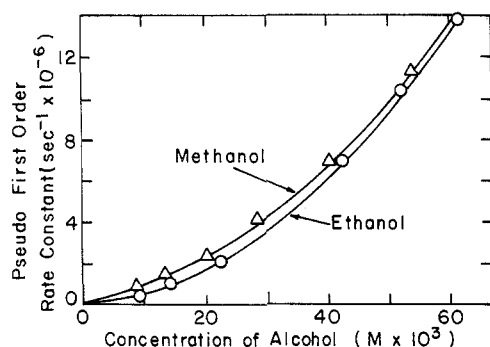
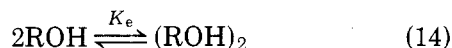


Figure 4. Plot of the pseudo-first-order rate constants for the reactions of benzhydryl cation with methanol (Δ) and with ethanol (\circ) in 1,2-dichloroethane at 24 °C against concentration of the alcohol.

are present not only in monomeric form but in higher aggregates as well. The deviation from linearity in Figure 4 may be understood in these terms if it is assumed that the reactivity of the carbenium ion is greater with the alcohol dimer than with the monomer. An analogous phenomenon in the case of protonation reactions of aromatic radical anions in dimethoxyethane has been encountered by Szwarc.³⁷ Assuming that only alcohol monomers and dimers, at equilibrium:



are kinetically significant, the differential rate equation for the decay of carbonium ion becomes

$$-d[\text{Ph}_2\text{CH}^+]/dt = (k_m[\text{ROH}] + k_d K_e [\text{ROH}]^2) [\text{Ph}_2\text{CH}^+] \quad (15)$$

k_m is the rate constant for reaction of the carbenium ion with alcohol monomer and k_d the rate constant for its reaction with alcohol dimer. The term $(k_m[\text{ROH}] + k_d K_e [\text{ROH}]^2)$ is the observed rate constant, k_{obsd} . Assuming the degree of dimerization is sufficiently small so that the monomer concentration may be represented, to a first approximation, by the alcohol concentration, a plot of $k_{\text{obsd}}/[\text{ROH}]$ vs. $[\text{ROH}]$ should give a straight line with slope $k_d K_e$ and intercept k_m . Such a plot for the reaction of benzhydryl cation with methanol and with ethanol is shown in Figure 5.

The values of the rate constant k_m , obtained from this treatment,¹⁸ or, in some cases, from the linear plot of the pseudo-first-order rate constant against alcohol concentration (benzhydryl cation reacting with 2-propanol shows little curvature) are shown in Table V. The values of $k_d K_e$ are $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for benzhydryl cation with methanol and with ethanol, 5×10^8 for benzhydryl with 2-propanol, and 2×10^8 for benzyl with methanol. It is not a simple matter to rationalize the higher reactivity of the alcohol dimer in terms of electron density on the oxygen in the dimer, or lower charge repulsion toward the carbenium ion. It is interesting, however, to note that the leaving group from the protonated ether intermediates is a proton in the case of the monomer and an alkoxonium ion (a bonded, stabilized state of the proton) in the case of the dimer.

Future Investigations

It is clear from the foregoing discussion that the pulse radiolysis method has been used effectively, and may continue to be used, in a broadening study of highly reactive carbanions and carbocations in solution. The

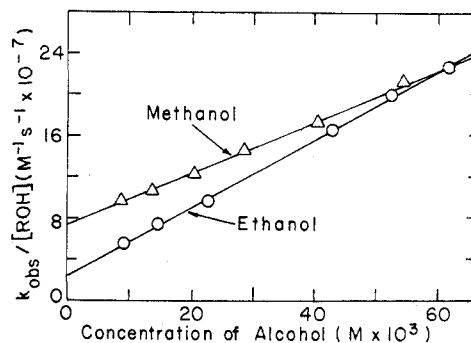


Figure 5. Plot of $k_{\text{obsd}}/[\text{ROH}]$ vs. $[\text{ROH}]$ for the reactions of benzhydryl cation with methanol (Δ) and with ethanol (\circ) in 1,2-dichloroethane at 24 °C.

Table V
Rate Constants for the Reaction of Arylcarbenium Ions with Aliphatic Alcohol Monomer in Dichloroethane at 24 °C

	$k_m, \text{M}^{-1} \text{s}^{-1} \times 10^{-7}$
$\text{Ph}_2\text{CH}^+ + \text{methanol}$	8
$\text{Ph}_2\text{CH}^+ + \text{ethanol}$	2
$\text{Ph}_2\text{CH}^+ + 2\text{-propanol}$	10
$\text{PhCH}_2^+ + \text{methanol}$	6
$\text{PhCH}_2^+ + \text{ethanol}$	10

observation in real time, with submicrosecond time resolution, represents a real advantage. The choice of solvent systems, particularly with respect to the absence or presence of chosen counterions, makes it a relatively straightforward matter to study the effects (both on the spectra and the kinetics) of ion pairing.

The initial work on benzyl carbanion has focused upon only a few aspects out of many possibilities. A strongly basic medium is not necessary for the formation, by this method (not even for those carbanions derived from very weakly acidic hydrocarbons), and investigations in solvents other than tetrahydrofuran are proceeding. The investigation of ion pairing is being extended. In this regard it is noteworthy that ion pairing with alkali metals may be restricted to the formation of the monomers of these organometallic species, avoiding the complications of higher aggregates which may be present in equilibrium systems.

The study of carbocations may be extended similarly to other solvents. In hydrocarbon solvents, however, it may be necessary to cope with the complication that both carbanions and carbocations are formed simultaneously. In the halogenated hydrocarbons, the kinetics of formation of the carbenium ions is being determined. Some effects of ion pairing are under investigation. Deuterium isotope effects are expected to be useful in determining whether deprotonation processes or hydride ion transfers are taking place.

Finally, it is hoped that we may extend the work to the observation of other carbenium ions by working at shorter wavelengths. The existence of an accessible optical absorption band is, of course, a necessary condition for direct observation, but the kinetics of some reactions may be determined equally well by monitoring the formation of product rather than the decay of the reacting species.

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