

Submicrosecond Formation and Observation of Reactive Carbanions¹

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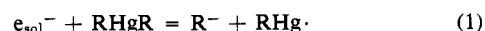
Abstract: The benzyl carbanion has been formed and studied in submicrosecond times by electron attachment to dibenzylmercury in tetrahydrofuran solution using the pulse radiolysis method. This carbanion has been studied in its sodium ion paired state, $C_6H_5CH_2^-Na^+$, and in its free state, $C_6H_5CH_2^-$, in the absence of sodium ion. The optical absorption spectra of both species were determined. The spectrum of the former is in agreement with previous observations, while that of the latter, which has heretofore not been observed, has an absorption maximum at 362 nm, with a molar extinction coefficient of $8300 M^{-1} cm^{-1}$ at the maximum. Absolute rate constants have been determined at 24° for the formation of both species: $C_6H_5CH_2^-$ is formed by the reaction $e_{sol}^- + (PhCH_2)_2Hg$, $2.7 \times 10^{10} M^{-1} sec^{-1}$; $C_6H_5CH_2^-Na^+$ is formed by ion pairing of the free carbanion with sodium ion, $PhCH_2^- + Na^+$, $1.5 \times 10^{11} M^{-1} sec^{-1}$, and by reaction of the sodium paired solvated electron with dibenzylmercury, Na^+ , $e_{sol}^- + (PhCH_2)_2Hg$, $7.9 \times 10^9 M^{-1} sec^{-1}$. Absolute rate constants for the proton transfer reactions of these carbanions from methanol, ethanol, ethanol-*O-d*, *tert*-butyl alcohol, and water have also been obtained. The values for $C_6H_5CH_2^-$ are: 2.3×10^8 , 1.4×10^8 , 1.2×10^8 , 1.6×10^7 , and $5.3 \times 10^7 M^{-1} sec^{-1}$, respectively. The values for $C_6H_5CH_2^-Na^+$ are: 5.8×10^9 , 3.7×10^9 , 2.1×10^9 , 1.3×10^9 , and $5.5 \times 10^9 M^{-1} sec^{-1}$, respectively. The observed isotope effect is discussed. Comparison is made of the relative rate constants for proton transfer to various carbon bases. This method of generating carbanions and of observing their fast reactions is of general applicability.

Carbanions are reactive intermediates of broad importance²⁻⁵ in organic chemistry. There is, consequently, great interest in the reactivity of this ionic species. Formation of reactive carbanions in solution, by an impulse method, which we report in this paper, makes it possible to observe them directly on a submicrosecond time scale, to determine their optical absorption spectra, and, more particularly, to evaluate absolute rate constants for many of their elementary reactions. The fast reaction method used is the pulse radiolysis method.⁶⁻⁸

Carbanions in solution have frequently been produced by the reduction of organomercury compounds. Alkali metal solutions have been used⁹ for this reduction, for the most part in equilibrium systems. Studies of hydrocarbon acidities have been carried out by electrochemical methods.^{10,11} In some systems,¹² fast reaction studies have been carried out by flow methods with

a resultant restriction on the time resolution in the range of milliseconds.

The present work follows upon our earlier studies^{13,14} in which aromatic radical anions were produced by electron attachment to aromatic hydrocarbons, upon pulse irradiation of solutions in polar liquids such as alcohols, amines, or ethers. Attachment of the solvated electron to organic halides in solution generally results in *dissociative* attachment giving the organic free radical and halide ion. Attachment to compounds such as naphthalene and anthracene is *nondissociative*, giving the aromatic radical anion. Attachment to organomercury compounds may be expected, on the other hand, to be *dissociative*, resulting in the formation of the carbanion and the organomercury radical.



Pulse radiolysis of such systems has now been carried out in tetrahydrofuran solutions. Rate constants have been determined for several protonation reactions of the benzyl anion, $C_6H_5CH_2^-$. We have carried out comparative studies of the effect of ion pairing on both the absorption spectrum and the reactivity of the carbanion since it is a matter of simple choice to produce the carbanion in an alkali metal ion paired state or free of cation pairing.

Experimental Section

The source of the electron pulse, as in our earlier studies,^{8,15} was a Varian V-7715A electron linear accelerator, delivering 3-4 MeV electrons at a pulse current of about 300 mA for a pulse duration of 100-1500 nsec and about 600 mA for a pulse duration of 80 nsec or less. Electron pulses of 20-80 nsec duration were used in this work. The transient optical absorptions were observed using an H.T.V. 196 detector with an S-1 response or an R.C.A. 1P28 with an S-5 response. A Bausch and Lomb grating monochromator, type 33-

(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.

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86-25, *f*/3.5, was used. Corning filters were used to eliminate second-order components from the analyzing light.

Our standard reaction cells,¹⁶ with high-purity silica windows and a cell length of 20.0 mm, were used with a double pass of the analyzing light beam.

The THF was purified first by refluxing under argon, for several hours, a solution containing benzophenone and excess sodium metal. This was followed by distillation through a glass bead packed column, the middle fraction being retained. It was then degassed and vacuum transferred into a bulb containing a mirror of freshly triple-distilled potassium. It was vacuum transferred from this bulb into the reaction cells just prior to the runs.

Dibenzylmercury (Alfa Inorganics) was recrystallized from ethanol, dried under vacuum, and stored in the dark until used. Ethanol (U.S.I. reagent quality), ethanol-*O-d* (Merck Sharp and Dohme), methanol (Eastman Spectro grade), and *tert*-butyl alcohol (Baker and Adamson reagent) were distilled from dissolved sodium metal into small storage bulbs. Water was triply distilled. The proton donors were degassed and vacuum transferred to the reaction cells as required. Sodium tetraphenylboron (Fisher reagent grade) was recrystallized as recommended¹⁶ and stored *in vacuo* until used.

Results and Discussion

Free Benzyl Anion. Carbanions, including benzyl anion, have been reported as intermediates in the reduction of the corresponding symmetrical diorganomercury compounds in electrochemical studies¹⁰ and in the form of the sodium paired benzyl carbanion by reduction of dibenzylmercury by sodium metal.⁹ One-electron reduction of organomercury halides, on the other hand, forms halide ion and the corresponding organomercury radical.¹¹ On the basis of this information, we expect the one-electron reduction of dibenzylmercury by attachment of the solvated electron, in our pulse radiolysis experiments, to proceed by dissociation to benzyl anion and benzylmercury radical as in reaction 1.

Our experiments lead to the observation of a transient uv absorption band which we assign to the free benzyl carbanion. This conclusion is based on the following observations: (1) that the solvated electron is indeed a precursor to the assigned transient band; (2) that the transient, in pairing with sodium ion, forms a second band which can be shown to be identical with the published⁹ optical absorption band of sodium paired benzyl carbanion; and (3) that the reactivity of the transient toward a series of proton donors is consistent with the comparable behavior of anions.

The decay of the solvated electron following irradiation, by an 80-nsec pulse, of tetrahydrofuran was monitored at 800 nm in the absence and presence of dibenzylmercury. This monitoring wavelength is at considerably longer wavelengths than the absorptions due to transient products of reaction 1. In pure THF the solvated electron decays principally by a second-order recombination with the solvent counterion with a rate constant¹⁷ of $2 \times 10^{12} M^{-1} \text{sec}^{-1}$. Under our experimental conditions, the first half-life of the solvated electron was roughly 500 nsec. With incremental dibenzylmercury concentrations from 9.6×10^{-5} to $3.8 \times 10^{-4} M$ the decay of the solvated electron became first order and the half-life progressively diminished. Pseudo-first-order rate constants, taken from plots of these rate curves, were linear in added substrate concentration

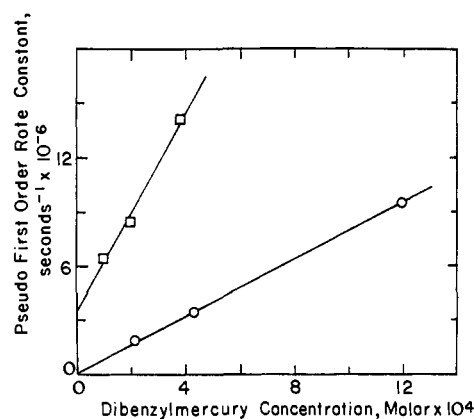


Figure 1. Plot of pseudo-first-order rate constants for decay of solvated electron vs. dibenzylmercury concentration: □, e_{sol} ; ○, $\text{Na}^+, e_{\text{sol}}^-$. Second-order rate constants taken from the slopes are $k_2 = 2.7 \times 10^{10}$ and $k_3 = 7.9 \times 10^9 M^{-1} \text{sec}^{-1}$ at 24° in THF.

over the range investigated. The second-order rate constant, obtained from data in Figure 1, is $2.7 \pm 0.8 \times 10^{10} M^{-1} \text{sec}^{-1}$. Attachment to dibenzylmercury is thus considerably slower than the dissociative electron attachment in THF¹⁸ to either *n*-butyl bromide ($6.9 \times 10^{10} M^{-1} \text{sec}^{-1}$) or *n*-butyl iodide ($1.1 \times 10^{11} M^{-1} \text{sec}^{-1}$) or the attachment to biphenyl ($1.1 \times 10^{11} M^{-1} \text{sec}^{-1}$).

Over the interval of observed electron decay, transient optical absorptions were detected and monitored at wavelengths shorter than 450 nm. The formation of the band centered at 362 nm, assigned to the benzyl carbanion (*vide infra*), followed approximate first-order kinetics. Only an upper limit for the rate constant of formation could be evaluated since a plateau in the formation curve was not clearly reached because of subsequent decay of the transient. The formation rate constant is $k < 4.4 \times 10^{10} M^{-1} \text{sec}^{-1}$, comparable to the more accurately determined electron attachment constant.

The separate bands which comprise the spectrum in Figure 2 exhibit a different time dependence. The decay at 311 nm is much slower than at 362 nm indicating that at least two species are generated by electron attachment to dibenzylmercury, as implied in reaction 1. The time dependence of the various bands is shown in Figure 2 by plotting the spectrum at zero time after the pulse, at 600 nsec when the short wavelength peak reaches its maximum optical density, and at 3.3 μsec when the rapid portion of the decay at longer wavelengths is complete.

The spectrum in Figure 2 may be reduced to a composite of three components; the two most strongly absorbing result from the reduction of the dibenzylmercury, while the third is produced from the THF alone. The band at 362 nm is effectively removed by proton donors such as alcohols and water as would be expected for a carbanion.

The shape of the band at 362 nm may be determined in three different ways. It may be extracted from the time-dependent spectrum in Figure 2 by subtraction of the spectrum at 3.3 μsec (normalized to the 311 peak) from the composite spectrum observed at $t = 0$. This difference spectrum is shown in Figure 3. It may also be extracted by adding an alcohol as scavenger to re-

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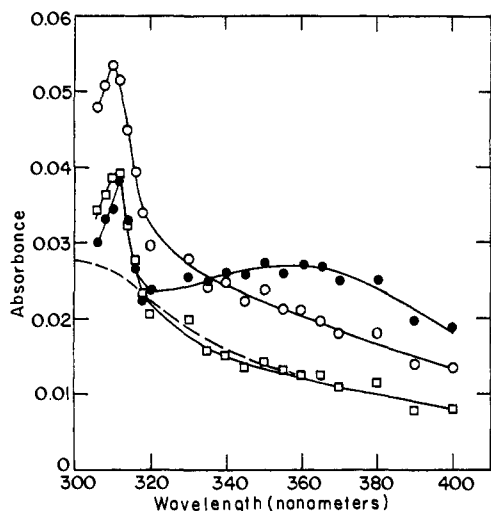


Figure 2. Transient absorption spectrum obtained following an 80-nsec pulse in a solution of $3.8 \times 10^{-4} M$ dibenzylmercury in THF: ●, $t = 0$ after pulse; ○, $t = 600$ nsec after pulse; □, $t = 3300$ nsec after pulse. The dashed line, a spectrum obtained separately by irradiating pure THF under similar conditions, has been added to reveal which components of the absorptions arise from attachment of the solvated electron. The different time dependencies of the 311- and 362-nm bands are apparent.

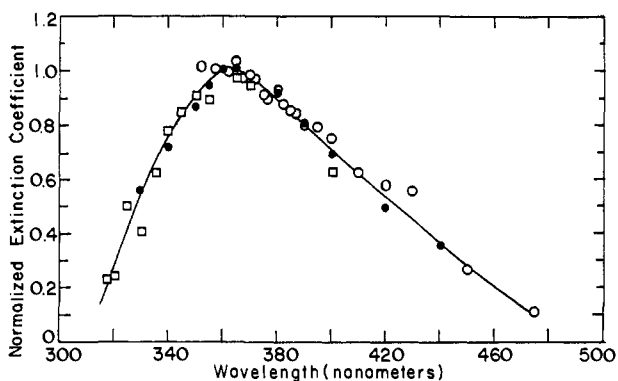


Figure 3. Normalized absorption spectrum of free benzyl carbanion in THF obtained by three independent methods: □, difference spectrum obtained from data contained in Figure 2; ○, difference spectrum obtained from transient spectra taken following an 80-nsec pulse in a solution of $1.9 \times 10^{-2} M$ dibenzylmercury with $5.5 \times 10^{-3} M$ methanol present; ●, spectrum obtained from observed absorption changes induced by sodium ion pairing and referred to $C_6H_5CH_2^-Na^+$ as explained in Figure 7. The wavelength of maximum absorption is 362 nm from the combined data.

move the carbanion peak more rapidly than observed in the absence of alcohol. This was done by irradiating a THF solution $1.9 \times 10^{-2} M$ in dibenzylmercury and $5.5 \times 10^{-3} M$ in methanol. A first-order decay of the 362-nm absorption band, with a half-life of 550 nsec, and the formation of a stable plateau were observed. Unfortunately, the higher concentration of substrate, while increasing the initial yield of benzyl anion, limited the transmission through the solution to wavelengths longer than 350 nm and the determination of band shape to the long wavelength portion. This extraction was again accomplished by subtracting the residual absorption at $t = 3 \mu\text{sec}$ from the absorption at $t = 0$. These data, also shown in Figure 3, are seen to be in reasonable agreement with the foregoing separation of the band. A third approach may be taken to the determination of the complete absorption band of the free

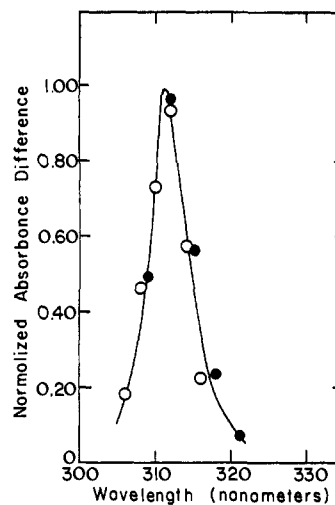


Figure 4. Normalized difference spectrum of the benzylmercury radical: ○, spectrum obtained from data contained in Figure 2; ●, spectrum obtained from transient absorptions following an 80-nsec pulse to a solution of $6.1 \times 10^{-4} M$ dibenzylmercury and $9.7 \times 10^{-3} M$ ethanol. The maximum of absorption is taken to be 311 nm, and the extinction coefficient is estimated to be $8000 M^{-1} \text{cm}^{-1}$ at the maximum.

benzyl anion and to evaluation of its molar extinction coefficient. This makes use of the published spectrum of the sodium ion paired benzyl anion and the measured spectral shift induced in the free carbanion absorption band upon ion pairing. The data obtained in this manner, as explained in the section on the sodium paired benzyl anion, are also shown in Figure 3. All three sets of data are in reasonable agreement, defining a transient band with a maximum at 362 nm, which reacts rapidly with proton donors, and which will be further shown, in a subsequent section, to be due to the benzyl anion.

With a defined spectral band at 362 nm in hand, the identity of the remaining spectrum created by electron attachment to dibenzylmercury may be established. The longer lived spectral component in Figure 2 is well represented as a composite of two intermediates: one resulting from the dibenzylmercury and one originating from the solvent itself. When pure THF was irradiated under comparable conditions a relatively weak, long-lived absorption, increasing toward shorter wavelengths, was found. This absorption persisted long after the absorption of the solvated electron¹⁷ had completely decayed. This absorption curve (normalized at its long wavelength plateau beyond 340 nm) was subtracted from the 3.3- μsec spectrum of Figure 2, giving a narrow band with a maximum at 311 nm. This 311-nm band is shown in Figure 4. It is apparent that this long-lived transient grows in during the electron attachment reaction. It is readily distinguishable from the spectrum of the benzyl radical¹⁹ with its two peaks at 305.5 and 317.1 nm which is not observed within the limits of our detection sensitivity. It seems reasonable to assign the 311-nm band to the $C_6H_5CH_2Hg\cdot$ radical fragment, the other product of reaction 1. We estimate its molar extinction coefficient to be $\epsilon = 8000 M^{-1} \text{cm}^{-1}$. This benzylmercury radical is stable, over at least a time of roughly 10 μsec , toward dissociation into benzyl radical (the yield of which must be below 0.01 molecule/100 eV)

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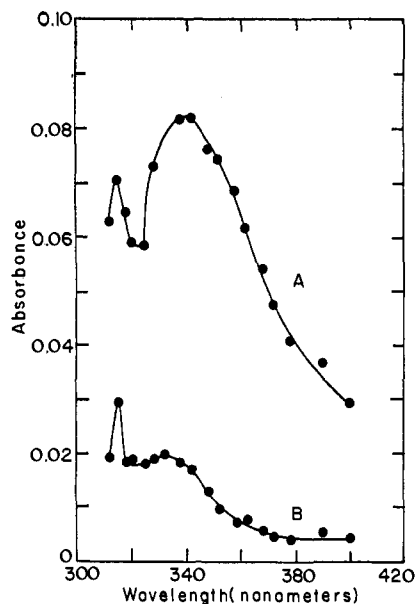


Figure 5. Transient spectra observed following an 80-nsec pulse in a solution of $1.2 \times 10^{-3} M$ dibenzylmercury and $1.0 \times 10^{-2} F$ sodium tetraphenylboron. Curve A, $t = 0$ after the pulse; curve B, $t = 1500$ nsec after the pulse.

and free mercury. This finding is in accord with the stability reported for organomercury radicals near the electrode surface in the electrochemical reduction²⁰ of organomercury halides. This 311-nm band has also been obtained with somewhat improved signal/noise ratio by irradiating a dibenzylmercury solution with added alcohol, a scavenger experiment analogous to that illustrated in Figure 3, with the exception that the substrate concentration was maintained at a low enough level to avoid complete absorption of the analyzing light at short wavelengths. Figure 4 contains these improved spectral results which are seen to be in reasonable agreement with the other set of data.

In contrast to the above results, the dissociation of dibenzylmercury upon one-electron *oxidation* in 1,2-dichloroethane, in related pulse experiments,²¹ yields the benzyl radical along with the benzyl cation which has λ_{max} 363 nm.

Sodium Paired Benzyl Carbanion. The transient absorption band with a maximum at 362 nm (Figure 3), which we identify as the free benzyl carbanion, obtained in the absence of sodium ion is very similar to the absorption band of the sodium paired benzyl carbanion. The latter, observed in sodium metal reduction experiments,⁹ has a band maximum at 355 nm. If we generate the free benzyl carbanion in the presence of sodium ion it couples very rapidly, as will be seen. Our pulse radiolysis experiments, when carried out in the presence of sodium ion, lead to a band in agreement with the published data⁹ for $\text{C}_6\text{H}_5\text{CH}_2^-\text{Na}^+$. The raw spectral data are shown in Figure 5, in which the spectrum obtained in a solution containing $1.2 \times 10^{-3} M$ dibenzylmercury and $1.0 \times 10^{-2} F$ sodium tetraphenylboron is shown at $t = 0$ after the pulse and at $t = 1.5 \mu\text{sec}$, when most of the carbanion band has decayed. The absorption band of $\text{C}_6\text{H}_5\text{CH}_2^-\text{Na}^+$ is obtained by

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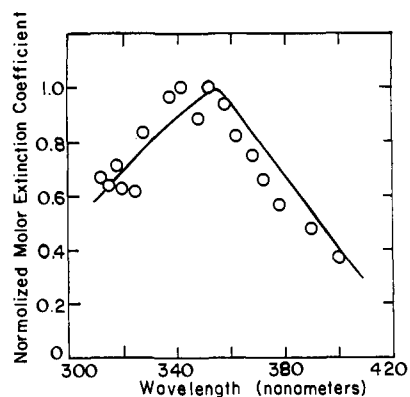


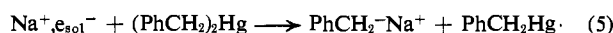
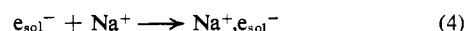
Figure 6. Spectrum of sodium ion paired benzyl carbanion in THF. The line is taken from the published spectrum;⁹ the points are taken from data contained in Figure 5. Both sets of data are normalized to the absorption maximum at 355 nm.

subtraction of the spectrum at $t = 1.5 \mu\text{sec}$ from the spectrum obtained at $t = 0$. The absorption band thus extracted is shown in Figure 6, where it is compared with the previously reported band⁹ for the sodium paired benzyl carbanion. Our data, while showing some scatter, seem to be in reasonably close agreement. There thus seems to be little doubt that we are forming the benzyl carbanion. It is formed in the unpaired state in the absence of sodium and in the paired state when sodium ion is present.

The sodium cation-benzyl carbanion pair may be formed by pairing of the free carbanion with sodium ion through the sequence



or by reaction of the sodium paired solvated electron¹⁸ with dibenzylmercury through the sequence



By appropriate choice of the concentration of free sodium ion we may, in view of reactions 2-5 and the interconversions they represent, determine: (a) the molar extinction coefficient of free benzyl carbanion based on the known extinction coefficient⁹ of $\text{PhCH}_2^-\text{Na}^+$; (b) the absorption spectrum of PhCH_2^- , in this case by comparative reference to the known spectrum⁹ of $\text{PhCH}_2^-\text{Na}^+$; and (c) absolute rate constants for reactions 3 and 5.

The molar extinction coefficient of the free benzyl carbanion may be determined from measurements of the change in optical density resulting from the ion pairing in reaction 3 as this reaction proceeds. This condition has been arranged by choosing $[\text{Na}^+]/[(\text{PhCH}_2)_2\text{Hg}]$ such that the solvated electron is scavenged entirely in reaction 2 and not at all by reaction 4 (the value of k_4 has been reported¹⁸). Under these conditions, reaction 5 is not taking place. If the reaction is observed at a wavelength for which $\epsilon_{\text{PhCH}_2^-} < \epsilon_{\text{PhCH}_2^-\text{Na}^+}$ the optical density will increase after the pulse; if $\epsilon_{\text{PhCH}_2^-} > \epsilon_{\text{PhCH}_2^-\text{Na}^+}$ the optical density will decrease after the pulse forming a plateau if the subsequent decay is slow enough. At a wavelength for which $\epsilon_{\text{PhCH}_2^-} = \epsilon_{\text{PhCH}_2^-\text{Na}^+}$ a horizontal straight line will result after

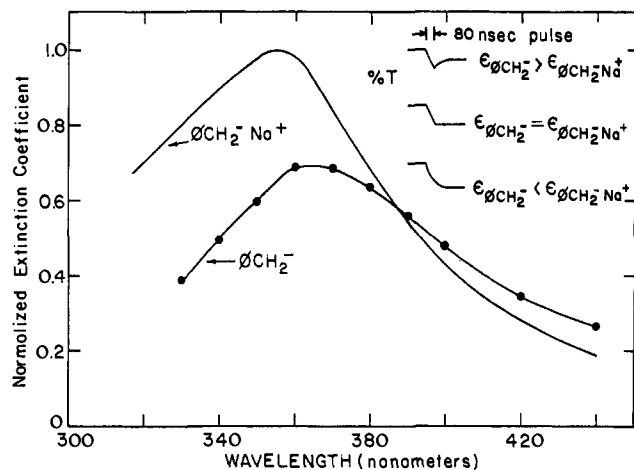


Figure 7. Effect of sodium ion pairing upon the optical absorption band of benzyl carbanion. The upper right-hand corner illustrates the various changes in the transient absorption observed at different wavelengths according to the relative magnitude of the extinction coefficients at those wavelengths. The changes following the 80-nsec pulse are coincident with ion pair formation by reaction 3. From these observations, the wavelength of equivalent extinction coefficients is 390 nm. The upper curve is from the published data.⁹ From this wavelength of equivalence and the published⁹ spectrum of $\text{PhCH}_2^- \text{Na}^+$, the spectrum of PhCH_2^- is constructed and its extinction coefficient at the maximum is found to be $8300 \text{ M}^{-1} \text{ cm}^{-1}$.

the pulse as shown in Figure 7. This wavelength of equivalence is 390 nm. From the spectra in Figures 3 and 6 and the value⁹ $\epsilon^{355}_{\text{PhCH}_2^- \text{Na}^+} = 1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ we obtain $\epsilon^{362}_{\text{PhCH}_2^-} = 8.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at the maximum.

The absorption spectrum of PhCH_2^- may also be obtained from data such as those in Figure 6 by measuring the magnitude of the increase or decrease in optical density over an interval of some 70 nsec following the pulse until a plateau is established corresponding to completion of reaction 3. The reaction was observed following irradiation with an 80-nsec pulse for a dibenzylmercury solution containing $1.2 \times 10^{-3} \text{ F}$ sodium tetraphenylboron ($2.8 \times 10^{-4} \text{ M}$ free sodium ion). Even at this relatively low concentration of free sodium ion the width of our pulse is not a negligible fraction of the time interval taken for completion of ion pairing. Accordingly, when using the change in optical density from the end of the pulse to the plateau to evaluate ϵ at any wavelength, we must take into account the extent of reaction 3 which has already transpired by the end of the pulse. A derivation of the appropriate equation to determine the extent of reaction during a rectangular pulse, which is applicable to our case, has recently been given.²² With this equation and the value we have determined for k_3 (*vide infra*), we calculate that, under our conditions, 67% of the ion pairing reaction has taken place by the end of the pulse. Under these conditions, the ratio of extinction coefficients is given in terms of the optical densities measured at the end of the pulse and at the plateau by the equation

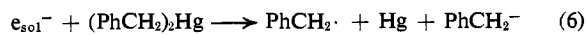
$$\frac{\epsilon^{\lambda}_{\text{PhCH}_2^-}}{\epsilon^{\lambda}_{\text{PhCH}_2^- \text{Na}^+}} = \frac{A_0 - A_{\infty}}{0.33A_{\infty}} + 1$$

The optical absorption band for the free benzyl carbanion may be found by evaluating $\epsilon^{\lambda}_{\text{PhCH}_2^-} / \epsilon^{\lambda}_{\text{PhCH}_2^- \text{Na}^+}$

(22) C. Capellos and B. H. J. Bielski, "Kinetic Systems," Wiley-Interscience, New York, N. Y., 1972, p 110.

at selected wavelengths over the appropriate range and relating these data to the spectrum⁹ for the sodium ion paired species. The spectrum obtained in this way is plotted in Figure 7. Good correlation is found among the spectral data obtained by three diverse methods, lending support to the quantitative validity of the data. Sodium ion pairing thus induces a hypsochromic shift of 7 nm in the band maximum of the free ion, comparable in magnitude and in the same direction as reported²³ for stable solutions of carbanions of related structure.

Although the primary evidence upon which the identification of the 362-nm band as PhCH_2^- rests is its conversion to $\text{PhCH}_2^- \text{Na}^+$, it is also useful to consider the possible dissociation reactions in the context of the fact that benzyl radical is not formed in any concentration above our limit of detection ($\sim 10^{-7} \text{ M}$ or $G \sim 0.01$ molecule/100 eV). The possible dissociation reactions are reaction 2 and



The absence of benzyl eliminates (6) and (7), establishes that PhCH_2Hg^- is not the precursor of $\text{PhCH}_2^- \text{Na}^+$ in the ion pairing reaction 3, and is thus consistent with the assignment and with the occurrence of (2).

Reaction Rate Constants. Absolute values for k_3 and k_5 have been determined. To determine k_5 we must simply impose the condition that the rate of reaction 2 is negligible relative to that of reaction 4 and then observe the decay of $\text{Na}^+, e_{\text{sol}}^-$ after a pulse. This condition obtains if $[\text{Na}^+]/[(\text{PhCH}_2)_2\text{Hg}]$ has an appropriate value based on the previously determined values of k_2 and k_4 . The dissociation constant of sodium tetraphenylboron in THF is known.¹⁶ At the highest dibenzylmercury concentration used, with sodium tetraphenylboron 0.012 F ($[\text{Na}^+] = 1 \times 10^{-3} \text{ M}$), $k_4' = 8 \times 10^8 \text{ sec}^{-1}$, while $k_2' = 3.2 \times 10^7 \text{ sec}^{-1}$, so that the formation of PhCH_2^- is negligible.

The decay of $\text{Na}^+, e_{\text{sol}}^-$ was monitored at 800 nm, near its absorption maximum of 890 nm, both in the absence and presence of dibenzylmercury over the concentration range 2.1×10^{-4} to $1.2 \times 10^{-3} \text{ M}$. At these concentrations the decay of $\text{Na}^+, e_{\text{sol}}^-$ is cleanly first order. The pseudo-first-order rate constants, calculated from the slopes of the first-order plots, are then plotted against dibenzylmercury concentration in Figure 1. The bimolecular rate constant $k_3 = 7.9 \pm 1.0 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ is calculated from the slope of this line. Comparison of k_3 with k_2 reveals that sodium ion pairing lowers the rate constant for attachment of the solvated electron to dibenzylmercury by roughly a factor of 3. The direction of this effect is consistent with that observed in earlier pulse studies of the reduction of aromatic compounds and alkyl halides.¹⁴

The determination of k_3 is also feasible as may be seen from consideration of the alternative sequence of reactions for $\text{PhCH}_2^- \text{Na}^+$ formation, namely, (2) and (3). Although the latter reaction induces a small blue shift in the absorption band maximum, determination of k_3 by following this shift is difficult because the magnitude of the change in optical density upon ion pairing is relatively small. Instead, k_3 is determined by observing the decay of PhCH_2^- under conditions for which $\text{PhCH}_2^- \text{Na}^+$ is removed as rapidly as it is formed in reac-

(23) J. Smid, "Ions and Ion Pairs in Organic Reactions," M. Szwarc, Ed., Wiley-Interscience, New York, N. Y., 1972, pp 85-151.

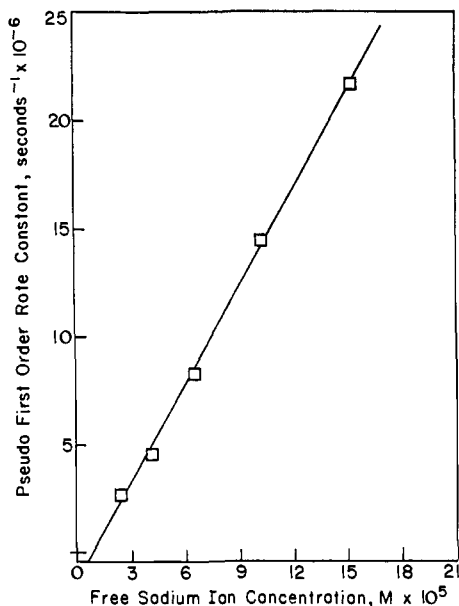
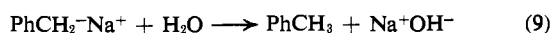


Figure 8. Pseudo-first-order rate constants for formation of the sodium cation benzyl carbanion pair from the free carbanion plotted *vs.* free sodium ion concentration. The second-order rate constant taken from the slope is $k_3 = 1.5 \times 10^{11} M^{-1} \text{sec}^{-1}$.

tion 3. This was done by using water as scavenger in the protonation reactions



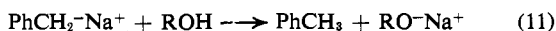
for which, as will be seen, $k_9 > 100k_8$. Thus, under conditions with $[(\text{PhCH}_2)_2\text{Hg}]/[\text{Na}^+]$ great enough (the opposite of that imposed in evaluating k_5) and with water present, reaction 3 becomes rate determining and may be observed directly.

k_3 was determined by irradiating a solution containing 0.02 M dibenzylmercury and free sodium ion over the concentration range 2.4×10^{-5} to 1.5×10^{-4} M with approximately 10^{-2} M water present. The decay of the 362-nm band of free benzyl carbanion in the presence of sodium tetraphenylboron was cleanly first order. The pseudo-first-order rate constants, obtained from the slopes of these plots, were linear in $[\text{Na}^+]$ over five incremental concentrations of free sodium ion as may be seen in Figure 8. From the slope of this line, we obtain $k_3 = 1.5 \pm 0.3 \times 10^{11} M^{-1} \text{sec}^{-1}$ at 24° . This value is very close to the rate constant reported²⁴ for the association of benzophenone ketyl radical anion with free sodium ion in THF ($1.1 \times 10^{11} M^{-1} \text{sec}^{-1}$) but lower than the rate constant for association of the solvated electron¹⁸ with sodium ion in THF ($7.9 \times 10^{11} M^{-1} \text{sec}^{-1}$).

Absolute rate constants for the proton transfer reaction of a series of aliphatic alcohols, as well as with water (reactions 8 and 9), were determined separately for each proton donor and independently for free benzyl carbanion, reaction 10, or sodium paired benzyl carb-



anion, reaction 11. This was done by irradiating sam-



ples with sodium tetraphenylboron absent or present in

(24) D. Beaumont and M. A. J. Rodgers, *Trans. Faraday Soc.*, **65**, 2973 (1969).

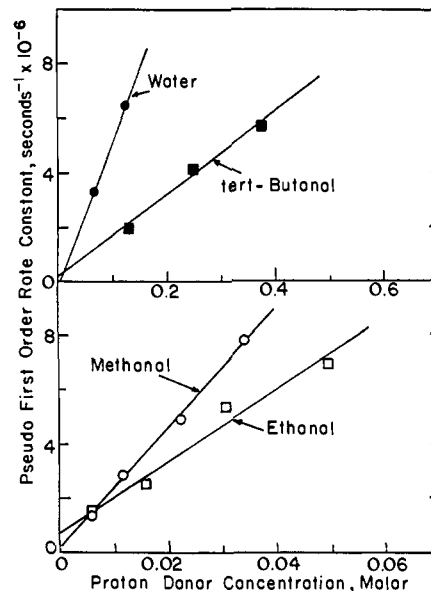


Figure 9. Pseudo-first-order rate constants for the decay of free benzyl carbanion in the presence of proton donors plotted *vs.* proton donor concentration. The second-order rate constants taken from the slopes are: CH_3OH , $k = 2.3 \times 10^8$; $\text{CH}_3\text{CH}_2\text{OH}$, $k = 1.4 \times 10^8$; $(\text{CH}_3)_3\text{COH}$, $k = 1.6 \times 10^7$; H_2O , $k = 5.3 \times 10^7 M^{-1} \text{sec}^{-1}$.

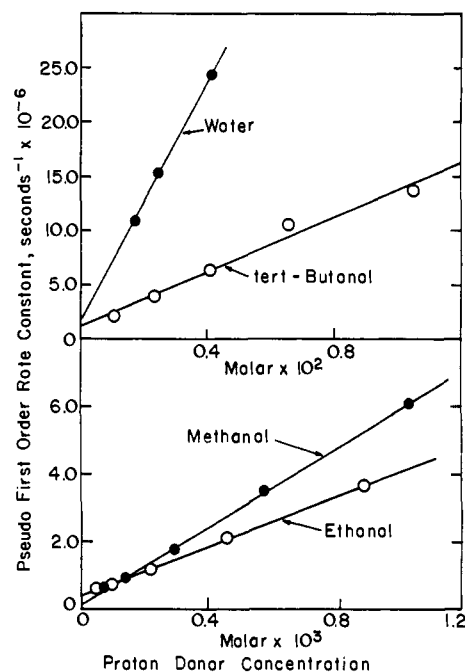


Figure 10. Pseudo-first-order rate constants for the decay of sodium ion paired benzyl carbanion in the presence of proton donors plotted *vs.* proton donor concentration. The second-order rate constants taken from the slopes are: CH_3OH , $k = 5.8 \times 10^9$; $\text{CH}_3\text{CH}_2\text{OH}$, $k = 3.7 \times 10^9$; $(\text{CH}_3)_3\text{COH}$, $k = 1.3 \times 10^9$; H_2O , $k = 5.5 \times 10^9 M^{-1} \text{sec}^{-1}$.

sufficient concentration to make the formation of the ion paired species compete overwhelmingly with the formation of the free benzyl carbanion. In both cases the decay of the carbanion was monitored at its absorption maximum in the absence and presence of incremental concentrations of the proton donor. These concentrations were sufficiently high to make the decay of carbanion cleanly first order. As may be seen in Figures 9 and 10, the pseudo-first-order rate constants obtained

are linear in the concentration of proton donor. Absolute rate constants, taken from the slopes of these plots, are gathered in Table I.

Table I. Rate Constants for Proton Transfer to Free and Sodium Ion Paired Benzyl Carbanion in THF at 297°K

Proton donor	$k_{\text{PhCH}_2^-}$, $M^{-1} \text{sec}^{-1} \times 10^{-8}$	$k_{\text{PhCH}_2^- \text{Na}^+}$, $M^{-1} \text{sec}^{-1} \times 10^{-8}$ ^a
Methanol	2.3 ± 0.3	58 ± 8
Ethanol	1.4 ± 0.2	37 ± 5
<i>tert</i> -Butyl alcohol	0.16 ± 0.02	13 ± 2
Water	0.53 ± 0.17	55 ± 7
Ethanol- <i>O-d</i>	1.2 ± 0.2	21 ± 3

^a 10^{-2} *F* sodium tetraphenylboron.

Table II. Relative Rate Constants for Proton Transfer to Various Carbon Bases

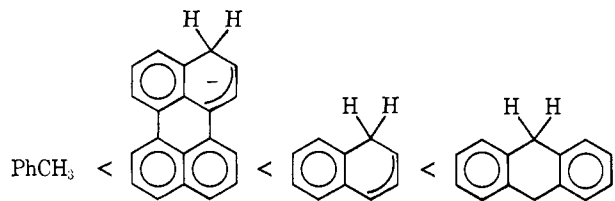
Donor	PhCH_2^- ^a	$\text{PhCH}_2^- \text{Na}^+$ ^a	A ^b	B ^c	C ^d
$k_{\text{CH}_3\text{OH}}$ (absolute)	2.3×10^8	5.8×10^9	1.05×10^1	1.2×10^6	2.0×10^6
CH_3OH	1.0	1.0	1.0	1.0	1.0
$\text{CH}_3\text{CH}_2\text{OH}$	0.60	0.64	0.68	0.65	0.20
$(\text{CH}_3)_2\text{CHOH}$			0.25	0.44	0.024
$(\text{CH}_3)_3\text{COH}$	0.07	0.23	0.060	0.093	
H_2O	0.23	0.96	0.23		

^a Solvent THF; this work; in units of $M^{-1} \text{sec}^{-1}$. ^b Solvent, dimethoxyethane; see ref 29b and A. Rainis, R. Tung, and M. Szwarc, *J. Amer. Chem. Soc.*, **95**, 659 (1973); in units of $M^{-1} \text{sec}^{-1}$. ^c Solvent, THF; see ref 28; in units of $M^{-1} \text{sec}^{-1}$. ^d Solvent, the pure alcohol; see S. Arai and L. M. Dorfman, *J. Chem. Phys.*, **41**, 2190 (1964). This absolute rate constant is given in units of sec^{-1} .

Several facts are immediately apparent from the data given in Table I. (a) The magnitude of the different rate constants lies in the relative order to be expected for an acid-base reaction in which the acidity of the proton donor, as has been measured in either 2-propanol²⁵ or in DMSO solution,²⁶ is varied. (b) Proton transfer from these donors, for free benzyl carbanion, is certainly far slower than diffusion controlled; even the rate constants for the ion paired species, while closer to the diffusion-control limit, still depend upon the acidity of the proton donor. (c) The free ion is less reactive than the ion pair by factors ranging from 20 to 100. (d) The deuterium isotope effects, although small, are not negligible, indicating that O-H bond breaking is involved at the transition state of the reaction. (e) The data indicate that the state of aggregation of the alcohol is not a factor in the kinetics, suggesting that there is a single reactive species.

In addition to the foregoing conclusions, some further information of interest may be obtained by comparison with the literature. In Table II, absolute rate constants for proton transfer from methanol to a variety of carbon bases in various solvents are given, along with the relative rate constants normalized to these values for methanol. The striking aspect of this comparison is that, in the two ether solvents, the carbanion, the sodium paired radical anion, and the sodium paired dianion all show very similar behavior, on a relative

basis, toward the proton donors. A Brønsted relationship²⁷ between $\log k$ and the pK differences seems to hold²⁸ with very nearly the same slope for each of these diverse acceptors over a range of more than seven orders of magnitude in k . On this basis, the conjugate acids of these hydrocarbon anions²⁹ may be placed in the following relative order of increasing acidity.



It seems possible that further work might add other examples to this series, thus placing acidities of transient intermediates on the same scale as the acidities of the more extensively studied hydrocarbons, perhaps even in a semiquantitative way.

The deuterium isotope effects for benzyl carbanion contained in Table I and those reported elsewhere for the conjugate base of each member of the foregoing acidity series reveal a relatively large effect for perylene dianion ($k_{\text{H}}/k_{\text{D}} = 7$) but small effects for sodium anthracene^{29b} and sodium naphthalene^{29a} as well as for benzyl carbanion ($k_{\text{H}}/k_{\text{D}} = 1.2$ to 1.7). Perhaps this large difference for perylene is to be correlated with the relative base strengths as has been indicated in experimental studies³⁰ of such isotope effects as well as from theoretical considerations.³¹ The experimental results have shown that the magnitude of the isotope effect exhibits a maximum as a function of relative base strength of the acceptor if this extends over a sufficiently wide range. The theoretical considerations correlate the isotope effect with the extent of proton transfer in the transition state suggesting that the greatest isotope

(27) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 564.

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

(29) (a) S. Bank and B. Bockrath, *J. Amer. Chem. Soc.*, **93**, 430 (1971); (b) S. Bank and B. Bockrath, *ibid.*, **94**, 6076 (1972). The rate constant reported for protonation by water in THF for sodium naphthalene is 16-fold greater than that for sodium anthracene.

(30) J. L. Longridge and F. A. Long, *J. Amer. Chem. Soc.*, **89**, 1292 (1967).

(31) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

(25) J. Hine and M. Hine, *J. Amer. Chem. Soc.*, **74**, 5266 (1952).
 (26) C. D. Ritchie, "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, p 230.

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

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.

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

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).