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Protonation Rate Constants and Optical Absorption Spectra of Benzyl Carbanion Pairs in Tetrahydrofuran Solution

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Abstract

The benzyl carbanion paired with lithium cation and with tetrabutylammonium ion has been formed in tetrahydrofuran solution and investigated by the pulse radiolysis method. Absolute rate constants for the protonation of both of these species by methanol and by t-butanol have been determined. These data, and previous data for benzyl sodium, show that the ion paired species is more reactive, in these protonations, than is the free carbanion. The optical absorption spectra of both $PhCH_2^-Li^+$ and $PhCH_2^-NBu_4^+$ were determined. The latter exhibits a band maximum at 342 nm, the former, in agreement with data from equilibrium studies, at 330 nm. The effect of ion pairing upon the absorption spectrum of $PhCH_2^-$ by Li^+, Na^+ and NBu_4^+ is shown.

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Effects of cation pairing upon the reactivity of aromatic radical anions[2-6] and carbanions[7-9] in solution have been demonstrated. In such studies both enhancement of rates and reduction of rates as a result of cation pairing have been found. In our recent report[7] of the formation and observation of benzyl carbanion on a submicrosecond time scale by the pulse radiolysis method[10,11], it has been shown how such studies may be extended to highly reactive carbanions. With this method the carbanions may be generated in either the unpaired state or in a cation paired state. In this report we extend these fast reaction studies of the benzyl carbanion, a relatively simple carbanion of particular interest in organic chemistry, to cover the effects of ion pairing with lithium cation and with tetrabutylammonium cation. These effects of cation pairing are concerned with changes in the optical absorption spectrum as well as with the reactivity of the species in elementary reactions. The particular reactions under investigation are protonation reactions with aliphatic alcohols.

Experimental

The source of the electron pulse, as in our earlier studies[12], was a Varian type 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 pulse duration less than 80 nsec. 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. The 10-90% rise time of these electronic detection systems was less than 10 nsec. A Bausch and Lomb grating monochromater, type 33-86-26, f/3.5 was used. Corning filters were selected to eliminate second-order components from the analyzing light beam. Our standard reaction cells[12], with high-purity silica windows and a cell length of 20.0 mm, were used with a double pass of the analyzing light beam.

Tetrahydrofuran, dibenzylmercury, methanol, and t-butanol all were purified as previously described[7]. Lithium perchlorate (Alfa Products, 99.5%) and tetrabutylammonium perchlorate (Eastman) were used as supplied after thorough drying under vacuum.

Results and Discussion

The formation of benzyl carbanion by electron irradiation of appropriate solutions occurs, as we have shown[7], when attachment of the solvated electron produces a dissociative ionization, as with dibenzylmercury in tetrahydrofuran:

$$e_s^- + (PhCH_2)_2Hg \rightarrow PhCH_2^- + PhCH_2Hg\cdot \qquad (1)$$

The rate constant[7] for this reaction is $2.7 \times 10^{10} M^{-1} sec^{-1}$. Since this dissociation is extremely rapid the use of an electron pulse with duration of 100 nsecs or less thus provides a ''pulse'' of benzyl carbanion. The carbanion may thus be formed in the absence of any pairing counterion or in the presence of selected cations by introducing, into the solution, dissociative salts. In the presence of a dissociative salt, M^+X^-, the corresponding ion pair of the carbanion may be formed in either of two ways:

$$M^+X^- \rightleftharpoons M^+ + X^- \qquad (2)$$

$$PhCH_2^- + M^+ \rightleftharpoons PhCH_2^-M^+ \qquad (3)$$

or

$$e_s^- + M^+ \longrightarrow (M^+, e_s^-) \qquad (4)$$

$$(M^+, e_s^-) + (PhCH_2)_2Hg \longrightarrow PhCH_2^-M^+ + PhCH_2Hg\cdot \qquad (5)$$

The particular path will depend upon the ratio $[M^+]/[(PhCH_2)_2Hg]$.

In the present study, the ion pairs of benzyl carbanion with lithium ion and with tetrabutylammonium ion have been formed by using $LiClO_4$ and NBu_4ClO_4 as the dissociative salt. In previous work[13-16] we have reported the absorption spectra of the primary reducing species in its various forms in THF, namely e_s^-, (Na^+, e_s^-) and (Li^+, e_s^-), as well as the values of the absolute rate constant, k_5, for both Na^+ ($7.9 \times 10^9 M^{-1} sec^{-1}$) and

Li^+ ($1.8 \times 10^{10} M^{-1} sec^{-1}$). There has been no evidence presented as yet that a process analogous to reaction (4) proceeds with NBu_4^+ in THF. In our system, the formation of $PhCH_2^-NBu_4^+$, for which we present evidence, occurs exclusively by the sequence of reactions (1) and (3).

The transient optical absorption spectra observed at the end of a pulse in solutions of dibenzylmercury and either $LiClO_4$ or NBu_4ClO_4 are shown in Figs. 1 and 2 respectively. The following evidence supports the identification of these absorption bands with the respective ion pairs, $PhCH_2^-Li^+$ (the spectrum of which is known in stable solutions) and $PhCH_2^-NBu_4^+$. The perchlorate salt concentration in these experiments was made great enough so that, whichever mechanism applies, the formation of the ion pair was complete by the end of the pulse. In the case of NBu_4^+, the ion pairing occured by reaction (3). In the case of Li^+, the ion pair formation occurred by way of the concurrent reactions (3) and (5). No continued formation of the ion pair was observed after the electron pulse.

The spectrum of $PhCH_2^-Li^+$, shown in Fig. 1, was derived from rate curves observed at various wavelengths following the irradiation of dibenzylmercury solutions with $LiClO_4$ (0.03F) present. In these solutions, which also contained either methanol or tert-butanol as carbanion scavengers, the absorption decayed in accord with a first order rate law, in less than 1 μsec to form a plateau. The decay is due to the protonation of the carbanion by the alcohol. The absorption plateau is undoubtedly due to radiolysis products other than the carbanion which decay with a much longer time constant than that observed for the foregoing protonation reaction. The absorption due only to the carbanion was determined by subtracting the absorbance values after the plateau is established from those at t=o after the pulse. The combined data from two separate experiments, using either alcohol, define an absorption band with a maximum at 330 nm which is undoubtedly due to $PhCH_2^-Li^+$ since the absorption maximum coincides with that reported for benzyl lithium from studies[17] in equilibrium systems. The potential in our method of formation lies in the ability to produce general ion pairs, R^-Li^+, in the monomeric form for the study not only of the spectra but of the absolute reactivity.

The transient absorption spectrum shown in Fig. 2 was obtained from dibenzylmercury solutions with NBu_4ClO_4 (0.01 to 0.02 F) present, in a manner similar to that described above using alcohol scavengers. The absorption maximum of the band is at 342 nm. On the basis of the manner of formation of this transient absorption and its reactivity toward the proton donors, we suggest that the species is $PhCH_2^-NBu_4^+$. The absorption is considerably removed from that for $PhCH_2^-$ (362 nm) and is different from the absorption of either $PhCH_2^-Li^+$ or $PhCH_2^-Na^+$. Different absorption spectra, depending upon the particular cation involved in ion pairing, have been found in earlier work with other carbanions[18]. The shift upon formation of the lithium ion pair is the largest observed among the three coupling cations, Na^+, Li^+ and NBu_4^+. Our spectra, although complete only on the low energy side because of cut-off of the transmission by dibenzylmercury, show that pairing with Li^+ narrows the band considerably. The halfwidth (on the low energy side) at half-height for $PhCH_2^-Li^+$ is about 2000 cm^{-1}, while for $PhCH_2^-$ it is about 4000 cm^{-1}. Ion pairing with Na^+ also narrows the absorption band, but not to as great an extent as with Li^+. Pairing with NBu_4^+, on the other hand, produces no discernible narrowing of the band.

Table I contains the absorption maxima of the three benzyl ion pairs and the free benzyl carbanion, along with similar data which have been reported for fluorenyl[18] ion pairs. It is noteworthy that, with the addition of our new data for $PhCH_2^-NBu_4^+$ to this series, a somewhat different order is found for the benzyl ion pairs than for the fluorenyl ion pairs.

Table I. Optical Absorption Band Maxima for the Free Carbanion and for Ion Pairs, with Various Cations, of Benzyl and Fluorenyl Ion in THF

Benzyl Carbanion		Fluorenyl Ion[b]	
Ion or Ion Pair	λ_{max} (nm)	Ion or Ion Pair	λ_{max} (nm)
$PhCH_2^-$	362[a]	Fl^-	374
$PhCH_2^-Na^+$	355[a]	$(Fl^-,M^+)_s$	373[c]
$PhCH_2^-NBu_4^+$	342	$Fl^-NBu_4^+$	368
$PhCH_2^-Li^+$	330	Fl^-Na^+	356
		Fl^-Li^+	349

(a) Reference 7

(b) Reference 18

(c) $(Fl^-,M^+)_s$ indicates a solvent separated ion pair for $M^+ = Li^+$ or Na^+, produced at slightly reduced temperatures.

Sodium ion pairing apparently has a greater relative effect upon λ_{max} for the Fl^-M^+ pairs than for the $PhCH_2^-M^+$ pairs.

The correlation between the nature of the cation and λ_{max} of the bands for Fl^-M^+, which have been identified as contact ion pairs, has been discussed[18] in terms of the radius of the counterion. It has been pointed out that greater shifts from λ_{max} for the free ion are induced by cations of smaller size. However, in the case of solvent separated ion pairs formed with alkali metal cations, the pairing induces somewhat less of a shift than has been found with NBu_4^+, a bulky ion with radius 4.5 A°, comparable to the dimension of the solvated cation in a solvent separated pair. If such a correlation may be applied to the ion pairs of benzyl carbanion, it reveals that Na^+ occupies the same relative position in the series as would a solvent separated ion pair, from which we infer that $PhCH_2^-Na^+$ in THF is a solvent separated pair. It is noteworthy that previous research[19] on polystyryl sodium, a somewhat similar carbanion pair, has led to the conclusion that PS^-Na^+ in THF is a contact ion pair. Apparently factors such as the degree of alkyl substitution at the benzylic position may determine the nature of the ion pair formed.

Absolute rate constants were determined for the proton transfer reaction of methanol and t-butanol to $PhCH_2^-Li^+$:

$$PhCH_2^-Li^+ + ROH \longrightarrow PhCH_3 + RO^-Li^+ \qquad (6)$$

and to $PhCH_2^-NBu_4^+$:

$$PhCH_2^-NBu_4^+ + ROH \longrightarrow PhCH_3 + RO^-NBu_4^+ \qquad (7)$$

The decay of the absorption of the carbanion pair was monitored, after an electron pulse, at the maximum of either carbanion species in both the absence and the presence of the proton donor. The solutions of dibenzylmercury irradiated had a sufficiently high salt concentration,

$[LiClO_4]$ = 0.04F or $[NBu_4ClO_4]$ = 0.02F, so that formation of the ion pair was complete before the proton transfer reaction was observed. The alcohol concentrations were sufficiently high to make the decay of the carbanion cleanly first order. The pseudo first order rate constants obtained are linear in the alcohol concentration, as may be seen in Figs. 3 and 4. The absolute rate constants, k_6 and k_7 (with an uncertainty of less than ± 20%) taken from the slopes of these plots, are shown in Table II along with previously determined values for $PhCH_2^-$ and $PhCH_2^-Na^+$ for comparison.

It is evident from these data that factors which determine the rate constant for each alcohol persist for all four forms of the benzyl carbanion which we have investigated. Thus, $k_{CH_3OH} > k_{t\text{-}C_4H_9OH}$ is the same order as the acidity of these alcohols as measured in DMSO[20], indicating that the acid-base nature of the reaction is rate determining. Further, the ion paired species, in all three cases, is more reactive than the free carbanion. The range of the kinetic effect produced by the ion pairing is considerably greater than that resulting from the dependence upon the proton lability for these two alcohols. It is interesting that the rate constants for protonation of a carbanion derived from even so weakly acidic a hydrocarbon as toluene are lower than the diffusion controlled limit.

It is interesting that sodium, while it has the largest rate enhancing effect of the three counterions, has the smallest effect upon the absorption spectrum. This slight effect upon λ_{max} was attributed to the formation of a loose, rather than a contact ion pair. We advance the speculation that the large rate enhancement may reflect the possibility that alcohol molecules may enter the primary solvation shell of the cation

Table II. Rate Constants ($M^{-1}sec^{-1}$) for the Protonation of the Benzyl Carbanion in its Various Forms by Aliphatic Alcohols in THF at 24°C

Benzyl Carbanion	CH_3OH	$t\text{-}C_4H_9OH$
[a]$PhCH_2^-Na^+$	5.8×10^9	1.3×10^9
$PhCH_2^-NBu_4^+$	6.0×10^8	4.6×10^8
$PhCH_2^-Li^+$	3.4×10^8	9.7×10^7
[a]$PhCH_2^-$	2.3×10^8	1.6×10^7

(a) Taken from reference 7

in a selective solvation, and are thus available for reaction; this close approach to the center of positive charge does not exist in the case of $\mathrm{NBu_4^+}$. Such specific solvation might also be expected for $\mathrm{Li^+}$ which, to the contrary, shows a relatively small rate enhancement. A different effect, the degree of polarity of $\mathrm{PhCH_2^-M^+}$, may be the determining factor for $\mathrm{PhCH_2^-Li^+}$. NMR studies[21] show that some degree of covalency exists for benzylithium, while we have reasoned that $\mathrm{PhCH_2^-Na^+}$ is solvent separated, and therefore completely ionic in character. It seems reasonable to suggest that the ability of $\mathrm{Li^+}$ to catalyze the proton transfer is reduced by the partial covalent nature of $\mathrm{PhCH_2^-Li^+}$ since this reduces the effective positive charge upon $\mathrm{Li^+}$.

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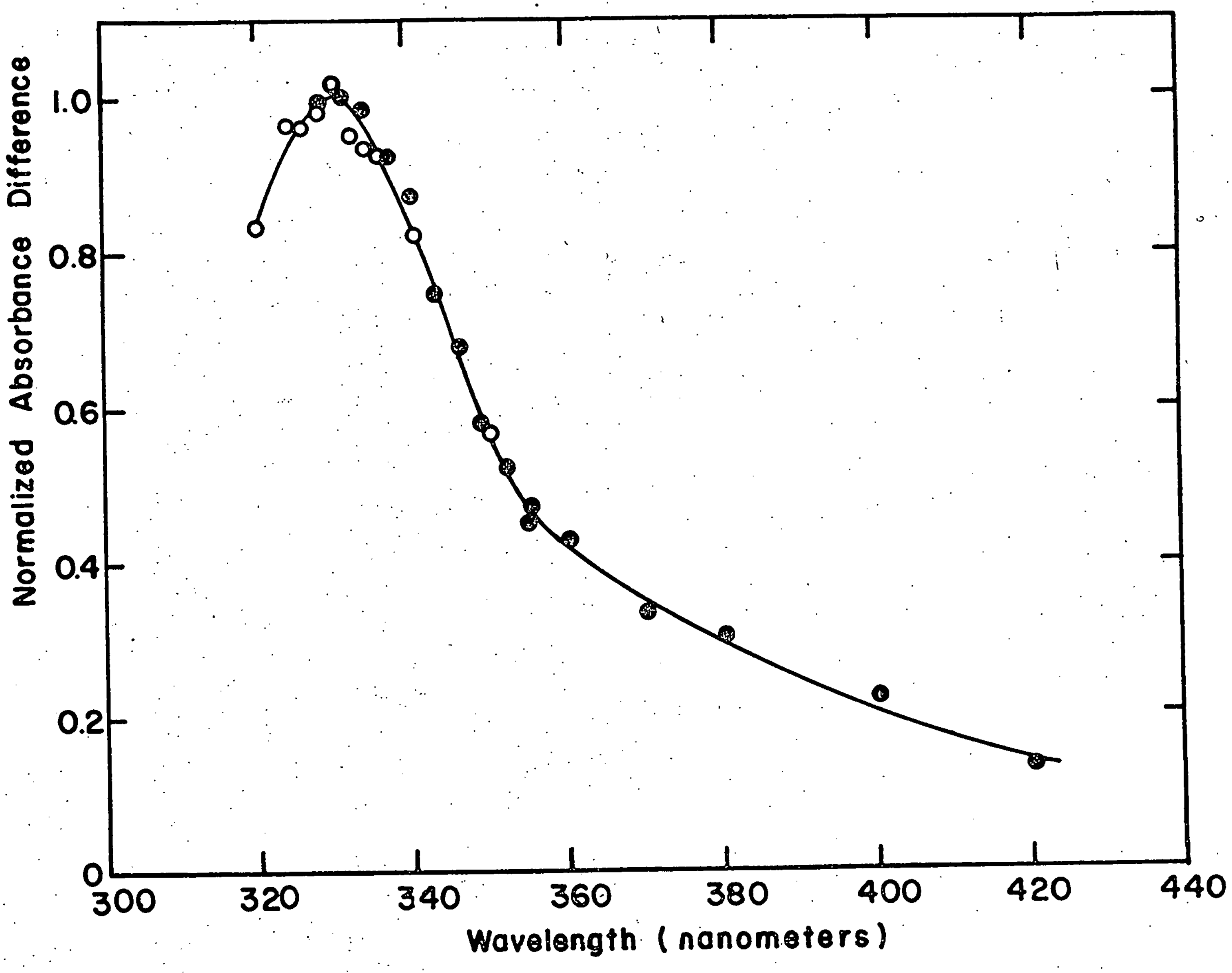
Figure Legends

Fig. 1. Normalized absorption spectrum of benzyl lithium in THF obtained from decay curves following irradiation of dibenzylmercury solutions with $LiClO_4$ (0.03F) present. The difference was taken between the absorption at t=o after the pulse and at t=1 μsec, when the protonation of the carbanion by the scavenger alcohol was complete: O, methanol (7.5×10^{-3}M); ●, t-butanol (2.0×10^{-3}M). From the combined data, the wavelength of maximum absorption is 330 nm, in agreement with the value[17] obtained in stable solutions.

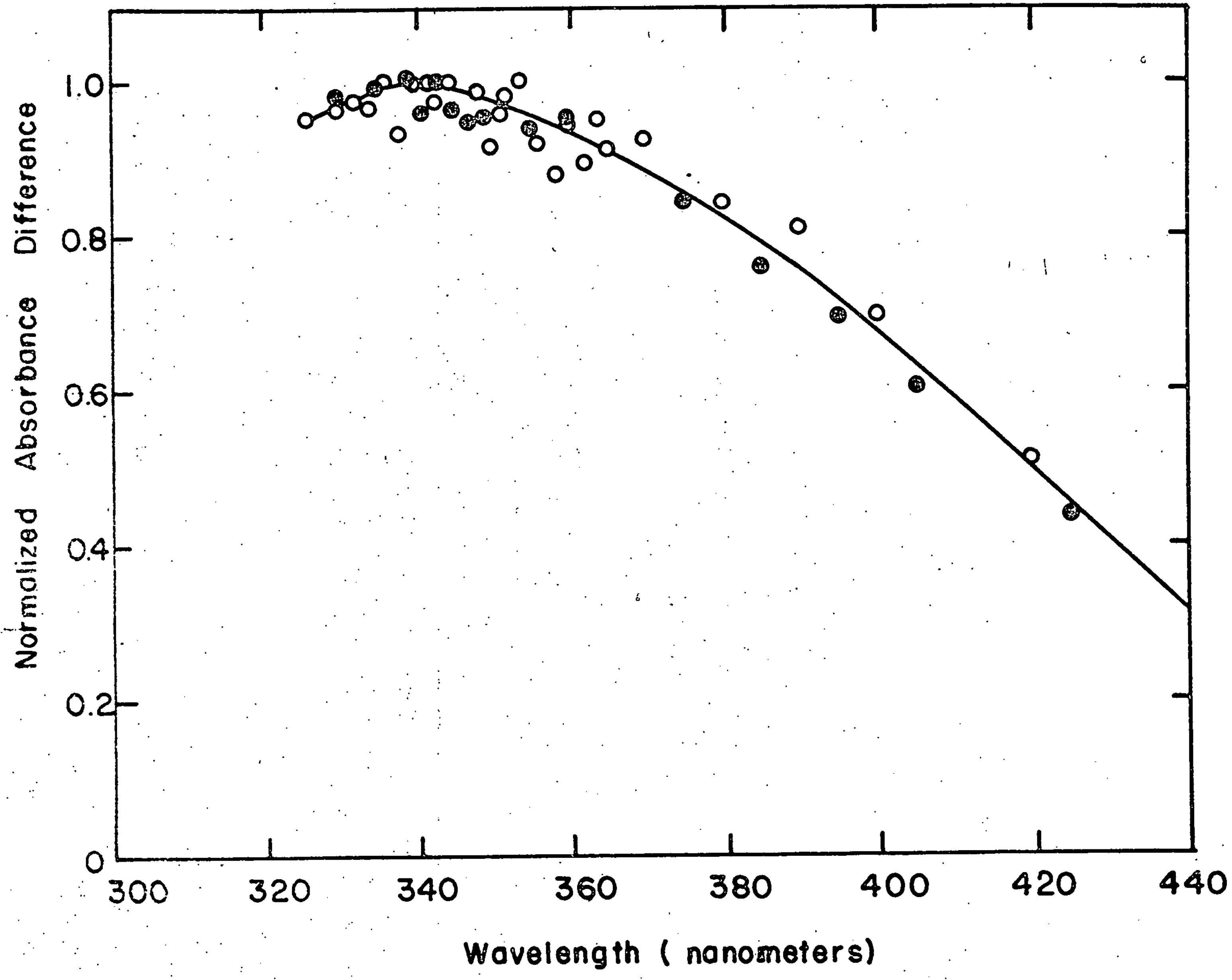
Fig. 2. Normalized absorption spectrum of $PhCH_2^-NBu_4^+$ in THF obtained from rate curves following irradiation of dibenzylmercury solutions with both NBu_4ClO_4 (0.01 to 0.02F) and a scavenger alcohol present: O, methanol (2.4×10^{-3}M); O, t-butanol (5.2×10^{-3}M). From these data, the wavelength of maximum absorption is 342 nm.

Fig. 3. Plot of pseudo first order rate constants for decay of benzyl carbanion pairs versus t-butanol concentration: O, $PhCH_2^-Li^+$; ●, $PhCH_2^-NBu_4^+$. Second order rate constants taken from the slopes are $k_6 = 9.7 \times 10^7$, and $k_7 = 4.6 \times 10^8\ M^{-1}sec^{-1}$, for t-butanol at 24^o in THF.

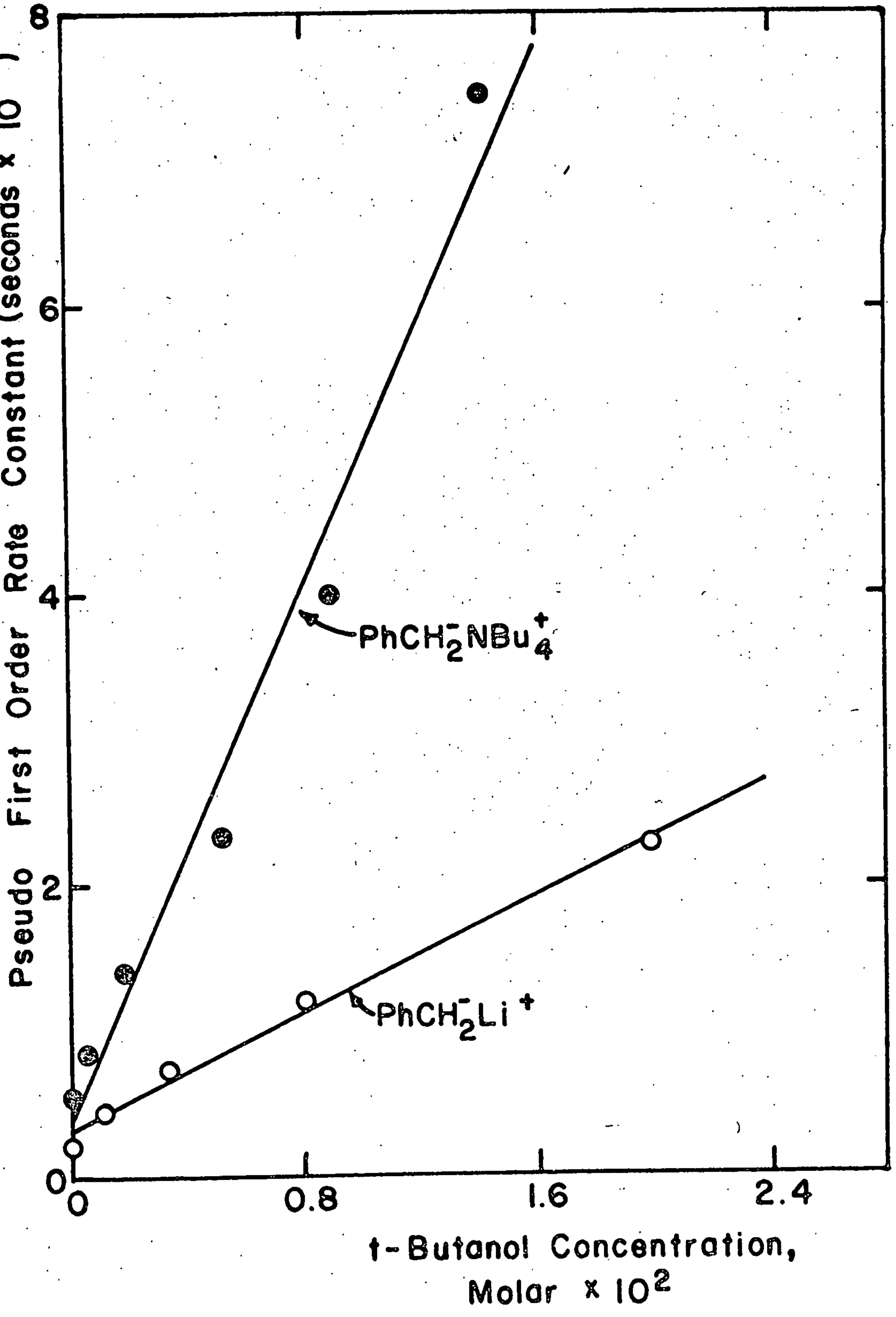
Fig. 4. Plot of pseudo first order rate constants for decay of benzyl carbanion pairs versus methanol concentration: O, $PhCH_2^-Li^+$; ●, $PhCH_2^-NBu_4^+$. Second order rate constants taken from the slopes are $k_6 = 3.4 \times 10^8$ and $k_7 = 6.0 \times 10^8\ M^{-1}sec^{-1}$, for methanol at 24^o in THF.



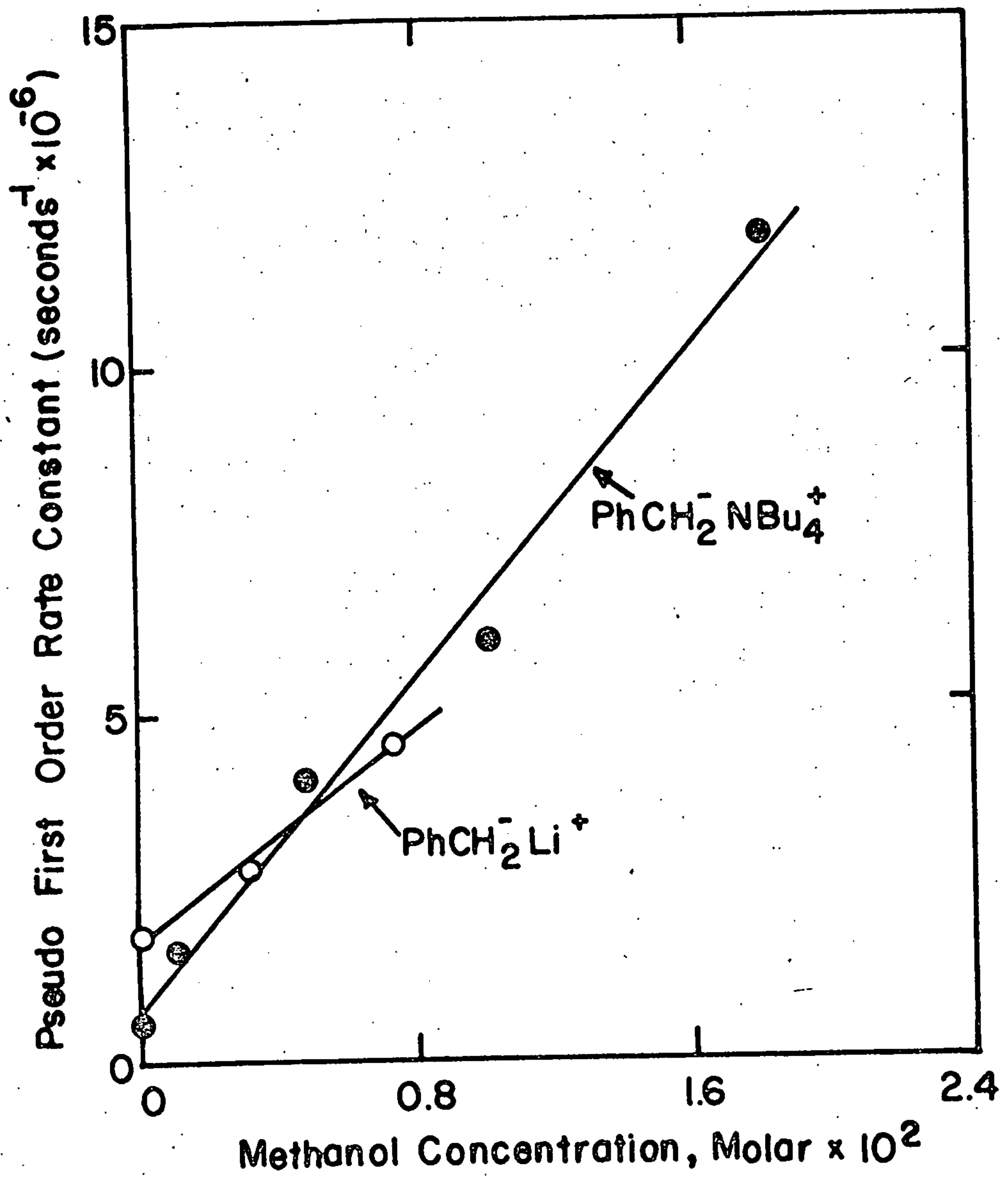
R -- DORFMAN Fig. 1.


Normalized Absorbance Difference
1.0
0.8
0.6
0.4
0.2
0
300
320
340
360
380
400
420
440
Wavelength (nanometers)

[illegible]



Bockrath and Dorfman, Fig 3



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