Solvation of Alkali 9-Phenylfluorenides in Mixtures of Tetrahydrofuran and Methanol

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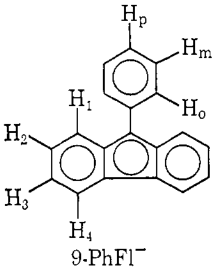
Abstract: Sodium and potassium 9-phenylfluorenide (9-PhFl$^-$) form contact ion pairs and lithium 9-PhFl$^-$ forms solvent-separated ion pairs at ambient temperature in tetrahydrofuran (THF), as determined by visible and nmr spectroscopy. In the presence of 1 equiv of dicyclohexyl-18-crown-6 ether, K^+9-PhFl$^-$ forms solvent-separated ion pairs. Addition of methanol to the ion pair solutions has little or no effect on the visible absorption maxima and the proton chemical shifts of 9-PhFl$^-$, but methanol protonates some of the 9-PhFl$^-$. The degree of protonation of 9-PhFl$^-$ by methanol depends on counterion, increasing in the order $K^+\cdot$ crown ether $< K^+ < Na^+ < Li^+$. The O–H stretching frequency of methanol in THF is not affected by K^+9-PhFl$^-$ or its crown ether complex. The delocalized carbanion 9-PhFl$^-$ is at best a slightly better hydrogen bond acceptor than THF, even though it is at least 18 pK units more basic than THF on conventional acidity scales.

Hydrogen-bonded carbanions have been hypothesized as intermediates to explain intramolecularity in a wide variety of base-catalyzed reactions, including allylic and related rearrangements, isoracemizations of carbon acids, and cleavages of alcohols and ketones.[1] However, independent thermodynamic and kinetic results indicate that methanol is a poor solvator of delocalized carbanions.[2] Specifically, fluoradene and other fluorenyl carbon acids are about 6 pK units more acidic in dimethyl sulfoxide (DMSO) than in methanol, and proton transfers to and from carbon are slower in methanol than in DMSO. In ether solutions alkali carbanides and alkali carbanion radicals derived from polycyclic aromatic compounds form ion pairs which have been studied by electronic, nmr, and esr spectroscopy.[3] In this paper I wish to report results of a search for hydrogen bonding between methanol and the 9-phenylfluorenide ion (9-PhFl$^-$) in tetrahydrofuran at ambient temperature by employing visible, infrared, and nuclear magnetic resonance spectroscopy.



9-PhFl$^-$

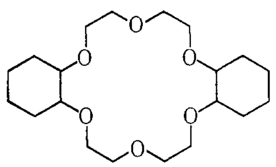
Results

Table I. Ultraviolet-Visible Spectra of M^+9-PhFl$^-$ Ion Pairs in THF at 25°

Cation	λ_{max}, nm (log ϵ)
Li^+	285 (4.46), 305 (4.28), 315 sh (4.22), 374 (4.23), 413 (4.36), 490 (3.37), 525 (3.26)
Na^+ [a]	306 (4.36), 375 (4.29), 392 (4.30), 491 (3.29) 522 sh (3.02)
K^+	281 (4.57), 305 (4.31), 373 (4.26), 397 (4.33), 475 (3.25), 490 sh (3.23), 5.25 sh (2.99)
$K^+\cdot$crown[b]	285 (4.58), 308 (4.33), 315 sh (4.31), 374 (4.27), 411 (4.37), 490 (3.38), 525 (3.25)
$(n\text{-}C_4H_9)_4N^+$ [c]	284 (4.56), 307 (4.30), 372 (4.27), 402 (4.34), 487 (3.30), 520 (3.15)

[a] Use of sodium dispersion in xylene for preparation prevented observation at <300 nm. [b] 1.06 mol of dicyclohexyl-18-crown-6 ether per mol of K^+9-PhFl$^-$. [c] Prepared by addition of 1.03 mol of $(n\text{-}C_4H_9)_4N^+B^-(C_6H_5)_4$ per mol of K^+9-PhFl$^-$.

Visible Spectra. Data for 9-PhFl$^-$ in THF at 25° appear in Table I. The Na^+, K^+, and $(n\text{-}C_4H_9)_4N^+$ 9-PhFl$^-$ may be designated as predominantly contact ion pairs, and the Li^+ and $K^+\cdot$ crown 9-PhFl$^-$ (prepared by addition of dicyclohexyl-18-crown-6 ether, 2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]hexacosane,[4] to K^+9-PhFl$^-$) may be designated as predominantly solvent-separated ion pairs by analogy to the work of Hogen-Esch and Smid on ion pairing of alkali fluorenides.[5] Their extensive investigation showed that solvent-separated alkali fluorenides (λ_{max} 373 nm) were favored over contact alkali fluorenides (λ_{max} 346–368 nm) by small cations, by low temperature, and by the cation-coordinating ability of ether solvents. In addition, Hogen-Esch and Smid demonstrated that both types of absorption maxima were due to ion pairs because of their lack of dependence on concentration and added common ion salts and because of their low conductivities.[5,6] The absorption maxima at 411–413



dicyclohexyl-18-crown-6 ether

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Table II. Dependence of K_{eq} on Cation and Concentration

Cation	Method[a]	Number of measurements	[M$^+$9-PhFl$^-$], *M*[b]	[CH$_3$OH], *M*	K_{eq}[c]
Li$^+$	Vis	3	2.8–5.7 × 10^{-4}	0.9–1.3 × 10^{-4}	4.1
Na$^+$	Vis	3	0.9–3.0 × 10^{-4}	2.7–8.9 × 10^{-4}	3.1
K$^+$	Vis	4	0.9–5.2 × 10^{-4}	0.010–0.16	7.2 × 10^{-3}
K$^+$·crown[d]	Vis	3	2.7–5.8 × 10^{-4}	0.15–0.25	2.0 × 10^{-3}
(n-C$_4$H$_9$)$_3$N$^+$ [e]	Vis	3	1.8–8.6 × 10^{-4}	0.25–1.7 × 10^{-1}	8.6 × 10^{-3}
K$^+$ [f]	Nmr	3	0.054–0.076	0.061–0.164	9.7 × 10^{-2}
K$^+$·crown[g]	Nmr	2	0.067–0.075	0.20–0.33	8.2 × 10^{-3}

[a] Measurements were made by visible or nmr spectroscopy. [b] In visible experiments [M$^+$9PhFl$^-$] + [9-PhFlH] = 1.00 × 10^{-3} *M*. [c] Median values with average deviations of ±40%. [d] The solution was 1.06 × 10^{-3} *M* in dicyclohexyl-18-crown-6 ether. [e] The solution also contained K$^+$B(C$_6$H$_5$)$_4^-$ and (n-C$_4$H$_9$)$_4$N$^+$ B(C$_6$H$_5$)$_4^-$. [f] [K$^+$9-PhFl$^-$] + [9-PhFlH] = 0.100 *M*. [g] [K$^+$9-PhFl$^-$] + [9-PhFlH] = 0.090 *M*; [crown ether] = 0.094 *M*.

nm for solvent-separated M$^+$9-PhFl$^-$ and at 392–402 nm for contact M$^+$9-PhFl$^-$ correspond to those used by Hogen-Esch and Smid to determine alkali fluorenide structure. Every value of λ_{max} in Table I was independent of M$^+$9-PhFl$^-$ concentration, within experimental error (±1 nm), in the range 10^{-4}–10^{-3} *M*. Consequently none of the spectra are of dissociated ions. The spectra reported here are similar but not identical with less complete spectra of Li$^+$ and Cs$^+$9-PhFl$^-$ in cyclohexylamine reported earlier.[7] The presence of methanol does not change λ_{max} values or relative extinction coefficients in any M$^+$9-PhFl$^-$ spectrum, but in large enough quantities methanol protonates 9-PhFl$^-$, forming 9-phenylfluorene (9-PhFlH) and alkali methoxide. In contrast, the strong solvating agents crown ether and DMSO readily convert contact ion pairs to solvent-separated ion pairs.[5,6] The failure of methanol to change visible spectra of M$^+$9-PhFl$^-$ indicates that methanol does not interact with the ion pairs or that its interactions with the ion pairs do not affect the spectra.

The amount of methanol required to protonate 9-PhFl$^-$ depends highly on the counterion and can be expressed in terms of eq 1, for which concentration equilibrium constants (K_{eq}) are reported in Table II.

$$\mathrm{M^+9\text{-}PhFl^- + CH_3OH \overset{K_{eq}}{\rightleftarrows} 9\text{-}PhFlH + CH_3O^-M^+} \qquad (1)$$

The absolute values of K_{eq} are not particularly meaningful because the relative acidities of methanol and 9-PhFlH depend on concentrations and because there was considerable scatter in the data. But relative values of K_{eq} most likely reflect the relative demands of cations for solvation.

Infrared Spectra. The position of the O–H stretching frequency of methanol hydrogen bonded to THF has been reported previously as 3483 cm^{-1} in carbon tetrachloride.[8] Data in Table III indicate that in THF, both in the presence and in the absence of K$^+$9-PhFl$^-$, ν_{OH} of methanol lies within experimental error of that value. No infrared measurements could be made with Li$^+$ or Na$^+$9-PhFl$^-$ because K_{eq} (eq 1) was too large. Hydrogen-bonded ν_{OH} values for methanol may vary over a range of 430 cm^{-1} and are dependent on the basicity and the structural type of the acceptor.[8] It is unlikely that ν_{OH} of methanol associated with 9-PhFl$^-$ would be experimentally indistinguishable from ν_{OH} of methanol associated with THF. The ir spectra show no sign of hydrogen bonding between methanol and 9-PhFl$^-$.

Table III. Infrared Spectra of Methanol in THF Solutions

[CH$_3$OH], *M*	Additives	Concn, *M*	ν_{OH}, cm^{-1} [a]
0.05–0.40			3484
0.05–0.39	K$^+$B(C$_6$H$_5$)$_4^-$	0.098	3483
	Crown ether	0.107	
0.06–0.16	K$^+$9-PhFl$^-$	0.05–0.09	
	9-PhFlH	0.02–0.03	3482
	K$^+$OCH$_3^-$	0.02–0.03	
0.10–0.33	K$^+$9-PhFl$^-$	0.07–0.08	
	9-PhFlH	0.01–0.02	3481
	K$^+$OCH$_3^-$	<0.004–0.012	

[a] Averages of 3–6 measurements with average deviation ±2 cm^{-1}.

Nmr Spectra. Chemical shifts of M$^+$9-PhFl$^-$ in THF at 27° are reported in Table IV, along with values for alkali fluorenides and alkali triphenylmethides used in assigning the spectra.[9] The assignments were confirmed by double irradiation experiments and by comparison of coupling constants for 9-PhFl$^-$ with those for fluorenide and triphenylmethide ions.[9,10] All spectra of 9-PhFl$^-$ fit a first-order description.

Examination of Table IV reveals two important points. First, the spectra of Li$^+$9-PhFl$^-$ and K$^+$·crown 9-PhFl$^-$, described as solvent-separated ion pairs at lower concentration by visible spectra, resemble one another; and the spectra of Na$^+$9-PhFl$^-$ and K$^+$9-PhFl$^-$, described as contact ion pairs by visible spectra, resemble one another. Second, changes in chemical shifts obtained by substitution of K$^+$ for Li$^+$ are nearly the same for the structurally similar protons in 9-PhFl$^-$, fluorenide, and triphenylmethide ions. Grutzner[9] found that contact and solvent-separated ion pair structures of alkali fluorenides could be assigned by relative dependencies of proton chemical shifts on solvent, cation, and temperature analogous to the conclusions of Hogen-Esch and Smid.[5] In this work cation, but not temperature and solvent, has been

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Table IV. Chemical Shifts of M$^+$9-PhFl$^-$ in THF at 27°

	δ in ppm downfield from TMS						
Ion pair	H_1	H_2	H_3	H_4	H_o	H_m	H_p
Li$^+$9-PhFl$^-$	7.845	6.850	6.494	7.866	7.683	7.111	6.584
Na$^+$9-PhFl$^-$	7.933	6.956	6.606	7.982	7.727	7.183	6.692
K$^+$9-PhFl$^-$	7.920	6.966	6.616	7.984	7.716	7.206	6.724
K$^+$·Crown 9-PhFl$^-$ [a]	7.894	6.888	6.532	7.914	7.732	7.133	6.608
Li$^+$$(C_6H_5)_3C^-$ [b]					7.275	6.484	5.925
Li$^+$ fluorenide[c]	7.2085	6.7135	6.331	7.8115			
K$^+$$(C_6H_5)_3C^-$ [b]					7.299	6.598	6.048
K$^+$ fluorenide[d]	7.2945	6.8135	6.4455	7.877			

[a] Solution was 0.079 *M* in K$^+$9-PhFl$^-$ and 0.094 *M* in crown ether. [b] Reference 9, p 141. [c] Reference 9, p 144. [d] Reference 9, p 145.

Table V. Effect of Methanol on Chemical Shifts of 9-PhFl$^-$ in THF at 27°

Ion pair		Methanol	Δδ[a]						
Cation	Concn, *M*	Concn, *M*	H_1	H_2	H_3	H_4	H_o	H_m	H_p
K$^+$	0.076	0.066	*b*	0.003	0.002	*b*	0.001	0.002	−0.001
K$^+$	0.068	0.16	*b*	0.014	0.003	*b*	0.008	0.004	0.001
K$^+$·crown[c]	0.075	0.20	0.002	0.002	0.001	0.002	0.002	0.002	0.002
K$^+$·crown[c]	0.067	0.33	*b*	0.005	0.004	*b*	0.004	0.005	0.003
K$^+$	0.080[d]								
K$^+$·crown	0.079[d]		0.026	0.078	0.084	0.070	−0.016	0.073	0.116

[a] δ(M$^+$9-PhFl$^-$ + CH_3OH) − δ(M$^+$9-PhFl$^-$) in parts per million downfield from TMS. [b] Value could not be obtained because of exchange broadening in presence of methanol. [c] Solutions were 0.094 *M* in dicyclohexyl-18-crown-6 ether. [d] δ(K$^+$·crown 9-PhFl$^-$) − δ(K$^+$9-PhFl$^-$) in parts per million downfield from TMS.

varied, and the results agree closely with the earlier investigations.[5,9]

The chemical shifts of 9-PhFl$^-$ were affected only slightly or not at all by the presence of methanol, as indicated in Table V. Equilibrium constants, K_{eq} (eq 1), were too large to permit study of interactions between 9-PhFl$^-$ and methanol when Li$^+$ and Na$^+$ counterions were used at nmr concentrations. Higher concentrations of methanol and K$^+$9-PhFl$^-$ also made values of K_{eq} for K$^+$9-PhFl$^-$ and K$^+$·crown 9-PhFl$^-$ determined by nmr higher than those determined by visible spectra (see Table II). Even with K$^+$·crown 9-PhFl$^-$ a large excess of methanol could not be employed because of extensive exchange broadening of the entire aromatic region of the spectrum. When K$^+$ is bound by crown ether, the methanol should change cation solvation least. So the shifts resulting from addition of methanol to K$^+$·crown 9-PhFl$^-$ more nearly reflect methanol's influence on 9-PhFl$^-$ than do the shifts for K$^+$9-PhFl$^-$. Changes in chemical shifts of the anion due to direct solvation should be as large as or larger than changes in chemical shifts of the anion due to solvation of its counterion. Since chemical shift differences between K$^+$9-PhFl$^-$ and K$^+$·crown 9-PhFl$^-$ are much larger than those resulting from addition of methanol to solutions of either type of ion pair, there must be little or no interaction between methanol and 9-PhFl$^-$. The nmr, ir, and visible spectra all support this conclusion.

Discussion

Nature of Ion Pairs or Aggregates. Previous results have demonstrated that electronic spectra of carbanide ion pairs are strongly influenced by solvent, cation, and and temperature.[5,6,11] The model of contact and solvent-separated ion pairs fits the observed spectra well, but other types of aggregates, whose spectra would be independent of concentration and common ion effects, cannot be ruled out. The nmr spectra of M$^+$9-PhFl$^-$ and earlier nmr results of Grutzner[9] were obtained at concentrations 10^2–10^3 times greater than those used for visible spectra. No data on concentration dependence of fluorenide ion or 9-PhFl$^-$ chemical shifts are available, but Grutzner's data on solvent, cation, and temperature dependence fit the ion pair model well. Other investigations by nmr have shown that the cations in lithium fluorenide and barium fluorenide lie above the plane of the fluorenide ion, but no state of aggregation was determined.[6c,10c,12]

Structure of Solutions. Once a model for alkali carbanide structure is assumed, the nature of solvation of cation, anion, and methanol comes into question. Methoxide ion, methanol, and THF as Lewis bases could solvate alkali ions. Solvation requirements are greatest for Li$^+$ and least for K$^+$, as demonstrated by the greater base strength of potassium alkoxides compared with sodium and lithium alkoxides in both thermodynamic and kinetic measurements.[13] The dependence of K_{eq} (eq 1) on cation in this investigation must be due to a much stronger association of Li$^+$ and Na$^+$ with methoxide ion than of K$^+$ with methoxide in DMSO, THF, and methanol solutions.[13] Measure-

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ments of boiling point elevation indicate that alkali methoxides are solvated by 5–9 methanol molecules in methanol and are highly aggregated in ethers and that methanol does a surprisingly poor job of breaking alkali methoxide aggregation in ethers.[13b,d] In this study only the visible spectra of K^+, $K^+\cdot$crown, and $(n\text{-}C_4H_9)_4N^+$9-PhFl$^-$ were examined in the presence of more than a ninefold excess of methanol over alkali methoxide and M^+9-PhFl$^-$, the amount required for complete alkali methoxide solvation in methanol.

Competing with alkali methoxide for methanol solvation must have been THF, a good hydrogen bond acceptor. Infrared spectra showed ν_{OH} only for methanol hydrogen bonded to THF. No attempt was made to detect a methanol–methoxide complex. In control experiments, Li^+ and Na^+ (in the form of tetraalkylborides) did not affect ν_{OH} of methanol in THF at salt concentrations of 0.1 *M* or less, but ν_{OH} was reduced at higher concentrations. Since cation shifts of ν_{OH} occurred only at >0.1 *M* salt, it is unlikely that methanol was associated with the cation in any other experiments reported here. The lack of influence of alkali ion or 9-PhFl$^-$ on ν_{OH} of methanol and the lack of influence of methanol on visible and nmr spectra of 9-PhFl$^-$ indicate that most or all of the methanol in these solutions associates with methoxide ion or THF, not with cation or carbanion.

To put the relative strengths of association of methanol with THF and with 9-PhFl$^-$ on a semiquantitative basis, let us assume from the chemical shifts of $K^+\cdot$crown 9-PhFl$^-$ with 0.33 *M* methanol (Table IV) that at most 10% of the 9-PhFl$^-$ is hydrogen bonded to methanol and that all remaining methanol is hydrogen bonded to THF. Application of these assumptions and the concentration data in Table V to eq 2, which

$$M^+\text{9-PhFl}^- + THF\cdot CH_3OH \rightleftharpoons M^+\text{9-PhFl}^-\cdot CH_3OH + THF \quad (2)$$

shows competition of THF and 9-PhFl$^-$ for methanol in simplified terms, indicates that the equilibrium constant for formation of a hydrogen bond to 9-PhFl$^-$ is at most four times that for formation of a hydrogen bond to THF. The relative abilities of THF and 9-PhFl$^-$ to accept a hydrogen bond contrast sharply with their relative basicities. On conventional scales, $THF\cdot H^+$ has p*K* = 2.1[14a] and 9-PhFlH has p*K* = 16.4[2b] or 18.6.[14b] Other investigators have found no correlation between base strength toward the proton and the ability to accept a hydrogen bond, except in structurally similar acceptors.[15] For their basicities delocalized carbanions are extremely poor hydrogen bond acceptors. Ritchie has reached the same conclusion from observations that fluoradene, 9-cyanofluorene, and 9-carbomethoxyfluorene were all stronger acids in DMSO than in methanol by about 6p*K* units and that proton transfers to and from carbon are slower in methanol than in DMSO.[2] In other terminology, delocalized carbanions are very soft bases and methanol is a very hard acid.[16] However, carbanions with charge localized in a lone pair of electrons may be much better acceptors of hydrogen bonds, a possibility which needs to be verified experimentally.

Hydrogen-Bonded Carbanions as Reactive Intermediates. Cram and coworkers have explained intramolecularity in a large number of base-catalyzed reactions by hypothesizing hydrogen-bonded carbanions as intermediates.[1,17] Solvent shifts of λ_{max} of alkali fluorenides in hydrazine and cyclohexylamine have been attributed to carbanion–amine hydrogen bonding by Petrov and Shatenshtein.[11d] The results of this paper indicate that methanol which is hydrogen bonded to a highly delocalized carbanion in methanol solution is thermodynamically unstable compared to self-associated methanol and unsolvated carbanion, because methanol hydrogen bonds to methanol more strongly than to THF ($\nu_{CH_3OH\cdot CH_3OH}$ = 3337 cm^{-1},[18] $\nu_{CH_3OH\cdot THF}$ = 3483 cm^{-1}).[8] Slow rates of proton transfer to and from carbon have been attributed to geometric rearrangement of structure during ionization and to failure of carbon acids and bases to fit into the hydrogen-bonding network of hydroxylic solvents, making solvent reorganization necessary for proton transfer. Slow solvent reorganization could be responsible for the intramolecularity of methoxide-catalyzed reactions in methanol also. No hydrogen bond between a highly delocalized carbanion and methanol is needed to explain intramolecularity of methoxide-catalyzed proton transfers in methanol. However, this conclusion cannot at present be extended to amine-catalyzed and other reactions in nonpolar solvents in which ion pairing can greatly increase intramolecularity.[1,17a,19] Also, polar substituents on delocalized carbanions may be strong enough hydrogen bond acceptors to increase intramolecularity of proton transfers.[1,17,19] Exploration of possible hydrogen bonding in ammonium carbanide ion pairs and to carbanions with polar substituents is planned.

Experimental Section[20]

Materials. 9-Phenylfluorene, mp 146.5–147.0°, was prepared by a literature method.[22] THF was distilled from calcium hydride under nitrogen and transferred to the drybox where it was distilled from potassium and K^+9-PhFl$^-$ immediately before use. Methanol was distilled from magnesium methoxide under nitrogen. Sodium tetraphenylboride was reagent grade. Lithium, potassium, and tetra-*n*-butylammonium tetraphenylborides were prepared from sodium tetraphenylboride.[23] Dicyclohexyl-18-crown-6 ether, mp 51–53°, a mixture of two isomers, was a gift from the Central Research Department of E. I. du Pont de Nemours and Company.[4] Potassium was cut into 0.1-g chunks, cleaned with *t*-butyl alcohol, blotted quickly, and stored in olefin-free, nitrogen-purged heptane. Sodium dispersion was prepared in olefin-free, nitrogen-purged decane and in xylene.[24] Lithium dispersion (30% in petrolatum, Lithium Corporation of America) was washed with olefin-free heptane until the washings were colorless.

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[20] All preparations and transfers of carbanion solutions were carried out in a drybox equipped with a drytrain designed according to Brown and coworkers.[21] All melting points are uncorrected.

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Preparation of Alkali 9-Phenylfluorenide Solutions. For visible spectra, 0.050 mmol of 9-PhFlH in about 30 ml of THF was treated under reflux for 4 hr with excess potassium or for 12 hr with excess lithium or sodium. The orange solutions were filtered through sintered glass and diluted to 50.0 ml, giving 1.00×10^{-3} *M* solutions. Methanol was added to 10-ml aliquots with a 1-μl syringe. For ir and nmr spectra, 0.50 mmol of 9-PhFlH, 3 ml of THF, and alkali metal were stirred for 4 hr at ambient temperature, filtered, and diluted to 5.00 ml, giving 0.100 *M* solutions. Methanol was added to 1-ml aliquots with a 1-μl or a 50-μl syringe. Solutions of K^+9-PhFl$^-$ for nmr investigation turned black during preparation, probably because of formation of the dianion radical of 9-PhFlH.[25] The nmr spectrum of one such solution was broadened beyond recognition, but addition of a negligible amount of methanol (0.025 *M*) restored the carbanion color and its nmr spectrum. Solutions were transferred to standard quartz uv cells and covered with serum caps, to standard 0.1-mm sealed sodium chloride ir cells with Teflon plugs, and to standard nmr tubes with polyethylene caps and stored in sealed containers.

Visible Spectra. All spectra were recorded on a Cary-14 instrument in cells of 0.5–50 mm path lengths. With each solution the regions 250–450 nm and 450–560 nm were examined in two cells whose path lengths differed by a factor of 10. Some samples deteriorated rapidly, probably because of air leakage through or around the serum caps.[26] Oxidation could be detected by appearance of absorption maxima at 312 and 271 nm, which do not occur in either 9-PhFlH or 9-PhFl$^-$. Data were discarded unless absorbances of a solution could be reproduced to within 5% in spectra obtained 60 min apart, and no band or shoulder appeared at 312 or 271 nm. The spectra reported in Table I are average values of λ_{max} and ϵ from at least two independent preparations. Equilibrium constants for methanol protonation of 9-PhFl$^-$ (Table II) are averages of at least three determinations. Concentrations of M^+9-PhFl$^-$ were obtained from eq 3 using ratios of absorbance of the solutions containing methanol to absorbance of the corresponding solution containing no methanol at two to four different absorption maxima. Concentrations of other species in solution were calculated by eq 4–6, in which the subscript 0 refers to concentration

$$[\mathrm{M^+9\text{-}PhFl^-}] = \frac{\mathrm{abs}}{\mathrm{abs_0}} \times 10^{-3}\,M \qquad (3)$$

$$[\mathrm{9\text{-}PhFlH}] = 10^{-3}\,M - [\mathrm{M^+9\text{-}PhFl^-}] \qquad (4)$$

$$[\mathrm{MOCH_3}] = [\mathrm{M^+9\text{-}PhFl^-}]_0 - [\mathrm{M^+9\text{-}PhFl^-}] \qquad (5)$$

$$[\mathrm{CH_3OH}] = [\mathrm{CH_3OH}]_0 - [\mathrm{MOCH_3}] \qquad (6)$$

prior to addition of methanol or to the sum of concentrations of methanol and methoxide in solution.

Infrared Spectra. A Perkin-Elmer 521 instrument was used under normal qualitative conditions except that the chart abscissa was expanded twofold and absorption maxima were scanned at 70 cm^{-1}/min. Frequency was calibrated with the 3027.1-cm^{-1} band of polystyrene. The hydrogen-bonded ν_{OH} was so broad that the frequency measurements had an average deviation of ± 2 cm^{-1}.

Nmr Spectra. A Varian HA-100 instrument with a Varian V-4315 frequency counter was used in the field sweep mode. All proton chemical shifts in 9-PhFl$^-$ were determined relative to the α-methylene resonance of THF which was used as the lock signal. After completion of the 9-PhFl$^-$ spectra, tetramethylsilane was added to the sample and the chemical shift of the THF α-methylene resonance was determined relative to TMS. All reported chemical shifts are averages of 4–8 measurements. No spectral changes of solutions were found after samples had stood for 24 hr at ambient temperature. Concentrations of M^+9-PhFl$^-$ and 9-PhFlH in solution were determined from integrated areas >4.00 and <4.00 ppm from THF, which are ratios of 6:7 and 2:11 for M^+9-PhFl$^-$ and 9-PhFlH, respectively. Concentrations of CH_3OH and CH_3OM were determined by eq 5–6.

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[26] On a preparative scale a solution of K^+9-PhFl$^-$ in THF was autoxidized to an intermediate which gave 9-phenyl-9-fluorenol after neutralization in 79% crude yield as reported earlier by Sprinzak.[27]

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Radiation-Induced Reactions of 1,3-Cyclohexadiene

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Abstract: Irradiation of 1,3-cyclohexadiene with γ rays leads to dimerization either in solution or in the neat liquid. Relative amounts of the products vary widely with reaction conditions but the composition of the mixtures can be expressed as consisting of variable amounts of two groups. One set of products corresponds to those formed in thermal dimerization and the other has the distribution found in photodimerization mediated by triplet sensitizers. Formation of the "thermal" dimers is inhibited by isopropyl alcohol, a cation scavenger, and promoted by electron scavengers so a cationic mechanism is postulated. Ring cleavage to give 1,3,5-hexatriene is also observed and attributed to an excited singlet state of the diene. Since ring opening is not affected by electron scavengers we infer that excited singlets are formed in primary excitation processes and that triplets are produced by charge neutralization.

In a continuation of high-energy radiation chemistry studies of photochemically reactive compounds[1,2] we have investigated the γ radiolysis of 1,3-cyclohexadiene in organic solution.

Evidence based on a large number of experiments involving chemical reactions,[1,2,3–8] scintillation stud-

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