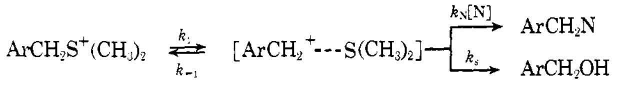
Table I. Rate Constants and Product Distributions of Reactions of Sulfonium Salts with Solvent and Added Nucleophiles in Water

Substrate		$M \times 10^3$	Added salt, M	Temp, °C	10^4k, sec^{-1}	% RN	10^4k_{calcd}, sec^{-1}
p-$CH_3OC_6H_4CH_2S^+(CH_3)_2$	ClO_4^-	7.83		60	1.78 ± 0.01		
	NO_3^-	6.60	$KClO_4$, 0.10	60	1.80 ± 0.01		
	NO_3^-	15.0		60	1.79 ± 0.03		
	NO_3^-	15.2	NaN_3, 0.030	60		51.5	
	NO_3^-	15.2	NaN_3, 0.060	60		71.3	
	NO_3^-	11.0	NaN_3, 0.070	60	2.64 ± 0.17	76.5	3.06[b]
	NO_3^-	15.2	NaN_3, 0.090	60		79.6	
	NO_3^-	6.60	NaN_3, 0.100	60	3.25 ± 0.30	82	3.23[b]
	NO_3^-	15.2	NaN_3, 0.120	60		84.7	
	NO_3^-	11.0	NaN_3, 0.120	60	3.50 ± 0.23	84.4	3.30[b]
$C_6H_5CH_2S^+(CH_3)_2$	ClO_4^-	7.82		150	3.36 ± 0.02		
	ClO_4^-	7.50		140	1.35 ± 0.01		
	NO_3^-	15.0		140	1.37 ± 0.03		
	ClO_4^-	15.0		140	1.35 ± 0.01		
	Br^-	7.50		140	2.25 ± 0.01		
	I^-	7.50		140	6.42 ± 0.07		6.09[c]
	NO_3^-	7.50	I^-, 0.0075	140	6.31 ± 0.19		6.09[c]
	I^-	7.50		140	6.43 ± 0.19		6.09[c]
	I^-	7.50	I^-, 0.0072	140	8.95 ± 0.10		8.96[c]
	I^-	15.0	I^-, 0.015	140	11.59 ± 0.11		12.3[c]
	I^-	15.0	I^-, 0.015	140	13.0 ± 0.5		12.3[c]
	I^-	15.0	I^-, 0.060	140	17.3 ± 0.8		16.2[c]
	ClO_4^-			60	0.000135[a]		
$(CH_3)_3CS^+(CH_3)_2$	ClO_4^-	7.5		75	2.32 ± 0.01		
	I^-	7.5		75	2.35 ± 0.01		
	N_3^-	7.5		75	2.35 ± 0.01	0	

[a] Extrapolated from data at higher temperatures. [b] Calculated assuming ion-dipole mechanism with $m = 48.0$ and $x = 1.19$. [c] Calculated assuming ion-dipole mechanism with $m = 655$ and $x = 14.3$.

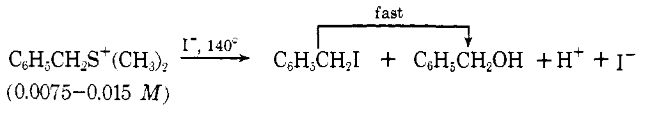
$H_2\cdots S(CH_3)_2]$, replaces the ion pair is suggested for these reactions of sulfonium salts. For this scheme, one



$$ArCH_2S^+(CH_3)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [ArCH_2{}^+{-}{-}{-}S(CH_3)_2] \begin{cases} \xrightarrow{k_N[N]} ArCH_2N \\ \xrightarrow{k_s} ArCH_2OH \end{cases}$$

derives the relationship[2] $k_{\text{exptl}}/k_{\text{NS}} = (x + 1)(1 + m[N])/(x + 1 + m[N])$, (NS = no salt), where, for Ar = p-methoxyphenyl and $[N_3^-] = 0.10$ at 60° in water, $k_{\text{exptl}}/k_{\text{NS}} = 3.25/1.78 = 1.82$ and $m = k_N/k_s = 48.0$ (from product data); whence $x = k_{-1}/k_s = 1.19$ and $k_1 = 3.90 \times 10^{-4}$ sec^{-1} (see Table I).

While the available data obtained utilizing the p-methoxybenzyl substrate can also be rationalized, albeit with difficulty, in terms of a competitive SN1–SN2 scheme, the kinetic facts which emerge from our study of the competitive reactions of water and iodide ion with benzyldimethylsulfonium ion (140°) cannot. Under these conditions, the initial product of iodide attack, benzyl iodide, is solvolyzed almost instantaneously to solvolysis product.[4] Further, since HI is a strong acid in water, the concentration of iodide ion



$$\underset{(0.0075\text{–}0.015\ M)}{C_6H_5CH_2S^+(CH_3)_2} \xrightarrow{I^-,\ 140°} C_6H_5CH_2I \xrightarrow{\text{fast}} C_6H_5CH_2OH + H^+ + I^-$$

remains constant throughout a run. Of particular significance among the data is the observation that the (pseudo-first-order) rate of reaction is less than first order in added iodide ion. Thus, while the first 0.0075 M increment of iodide ion effects a rate enhancement of *ca.* 5×10^{-4} sec^{-1}, it requires approximately three additional increments of 0.0075 M iodide to enhance the rate an additional 5×10^{-4} sec^{-1}. It will be realized that a competitive SN1–SN2 mechanism predicts a linear increase in the rate constant with iodide concentration. The ion-dipole mechanism, with $m = k_N/k_s = 655$ and $x = k_{-1}/k_s = 14.3$, achieves an excellent correlation of the data (see Table I).

The nature of the ion-dipole assemblage is worthy of some consideration. We envisage it as a close analog of an ion pair, the dimethyl sulfide molecule interacting strongly with the carbonium ion center, $R^+\cdots S(CH_3)_2$. Both because of its high nucleophilicity (relative to water) as well as because of its probably preferred orientation for return to sulfonium ion (microscopic reversibility), collapse should occur fairly readily. With increasingly stable carbonium ion centers (as, for example, p-methoxybenzyl), diffusion of the dimethyl sulfide into the bulk of the solvent should begin to compete more effectively with collapse, resulting in a decreasing value of $k_{-1}/k_s = x$, as is observed experimentally.

Richard A. Sneen,* G. Robert Felt, William C. Dickason
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received July 17, 1972

---

(4) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).

Ultraviolet-Visible Spectroscopic Evidence for Hydrogen-Bonded Alkali Carbanions in Protic Media

Sir:

Considerable information has become available in the last few years on the structure of alkali and alkaline earth carbanions and radical anions in aprotic media.[1] Much less is known in any detailed way about the solvation of these type ions and ion pairs in protic media. Extensive work on the stereochemistry of a variety of

---

(1) M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Interscience, New York, N. Y., 1968, Chapter V.

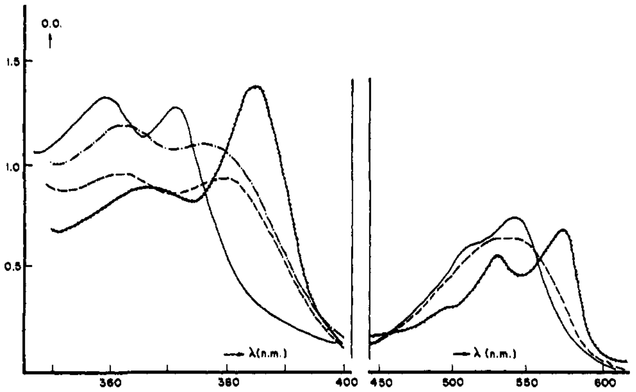


Figure 1. Fluoradenyl–sodium absorption spectra in THP, *n*-propyl alcohol, and 1:1 THP–*n*-propyl alcohol mixtures at 23 ± 1° ($[FD^-Na^+] \simeq 10^{-3}$ to 5×10^{-4}) (spectra do not indicate relative values of extinction coefficients): (——) Na^+FD^-–THP; (- - -) Na^+FD^- in 50% THP–*n*-C_3H_7OH; (—·—) Na^+FD^-–*n*-C_3H_7OH (or CH_3OH); (–•–•–) $(NaCE)^+FD^-$ in 50% THP–*n*-C_3H_7OH.

reactions involving carbanions as intermediates suggests the existence of H-bonded carbanions in a variety of protic media.[2] However, attempts to demonstrate these species spectroscopically in THF–CH_3OH (up to 0.4 *M* in CH_3OH) mixtures were unsuccessful.[3] It was, therefore, thought of interest to investigate these systems in the presence of larger concentrations of alcohol in order to avoid competitive H bonding by ether. The anion of fluoradene[4] was selected as the uv–visible spectroscopic probe because of the high acidity of the hydrocarbon ($pK_a \simeq 11$) making spectral observation at high alcohol concentration possible and because of the suitability of its fluorenyl-type anion (FD^-) as a probe for ion pairing.[5] Thus red shifts are observed on increasing the cationic radius in solvents where only contact ion pairs exist (Table I). On adding crown ethers such as dimethyldibenzo-18-crown-6 (CE) to the K^+ salt in tetrahydropyran (THP), the conversion of contact to separated ion pairs can clearly be observed (Table I).

The spectra of the unpaired carbanion in the high dielectric constant solvents DMSO ($\epsilon = 45$) and HMPA ($\epsilon = 30$) are identical with the spectra of separated ion pairs in low dielectric constant solvents such as THF (FD^-Li^+) and DME (FD^-Na^+) as was previously found for fluorenyl anion.[5b] In protic media such as methanol, ethanol, and 1-propanol, however, the FD^- spectra are substantially broadened and blue shifted, 12 nm (388 → 376 nm) in the uv and 20 to 30 nm in the visible region where the three separate peaks have merged into a wide band with a maximum between 525 and 540 nm (Table I). These spectra cannot be due to partial ion pairing because of absence of common ion effect. Since no reasonable correlation of the observed shifts in aprotic and protic solvents can be found with existing solvent polarity parameters such as dielectric constant or *Z* values,[6] it seems that nonspecific carbanion solvation is not responsible for the observed shifts. The observed new band at 376 nm is then most likely due to specific solvation of carbanion by alcohol such as hydrogen bonding. This interpretation is supported by similar but smaller shifts observed in the less acidic amines (Table I). Larger blue shifts (≃10 nm in the visible region) have been reported for the more strongly basic fluorenyl anion in cyclohexylamine.[7]

Table I. Near Uv and Visible Absorption Maxima of the Fluoradenyl Carbanion Alkali Salts in Protic and Aprotic Media[a]

System	Ion pairing[g]	ϵ[f]	Maxima
FD^-Li^+, THF	Ssip	7.4	369, 388, 529, 570
FD^-Na^+, THF	Ssip, cip	7.4	361, 371, 388, 530, 570
FD^-K^+, THF	Cip	7.4	363, 376, 520, 553
FD^-Na^+, THP	Cip	5.6	359, 371, 510, 540
FD^-K^+, THP	Cip	5.6	361, 374, 512, 547
FD^-Na^+ (K^+) in CH_3OH, C_2H_5OH, *n*-C_3H_7OH	Free ions	32.5–20.1	361, 376, 525–540[b]
In $H_2NCH_2CH_2NH_2$	Ssip	≃16	368, 386, 525, 565
FD^-CENa^+, (K^+) THF (THP)	Ssip	7.4 (5.6)	369, 388, 530 570
FD^-CENa^+, THP–*n*-C_3H_7OH[d]	Ssip	13.6[c]	367, 386, 525, 567
FD^-Na^+, THP–*n*-C_3H_7OH[d]	Ion pairs	13.6[c]	362, 380, 525–540[b]
FD^-Na^+, THF–*n*-C_3H_7OH[e]	Ssip	12.6[c]	369, 388, 530, 568
FD^-H_3N–*n*-C_3H_7OH–*n*-$C_3H_7NH_2$	Ion pairs	≃6	361, 376, 525–540[b]
Same with small excess CE	Ssip	≃6	367, 386, 525, 567

[a] Measured at 23 ± 1°. [b] Broad maximum between these values. [c] Calculated on a mole fraction basis. [d] 50 vol % *n*-C_3H_7OH. [e] 40 vol % *n*-C_3H_7OH. [f] Dielectric constants. [g] Ssip, Cip—solvent-separated and contact ion pairs, respectively.

Additional evidence was obtained by examining the spectrum of the *n*-propylammonium salt of fluoradene, prepared by dissolving the hydrocarbon in *n*-propylamine under high-vacuum conditions.[8] The resulting spectrum is essentially the same in uv and visible regions as that obtained in alcohol (Table I). This spectrum is not due to carbanion solvation since it differs substantially from the Na^+ and K^+ salts in amines in λ_{max} and band width (Table I). On addition of a small excess of CE to the ammonium carbanion salt, the bands narrow appreciably and give a spectrum that closely resembles that of separated ion pairs (Table I).

$$FD^- \cdots H_3N^+\text{-}C_3H_7 + CE \rightleftharpoons FD^-[CEH_3N\text{-}C_3H_7]^+$$

Further evidence for the proposed H bonding in these systems is indicated by titration experiments of FD^-Na^+ in THP–*n*-C_3H_7OH mixtures. On addition of alcohol a new broadened band close to 380 nm is observed simultaneous with the original absorption at 370 nm. On increasing the alcohol concentration, this new band increases in relative intensity.[9] At about 50 vol % of

---

(2) (a) J. N. Roitman and D. Cram, *J. Amer. Chem. Soc.*, **93**, 2231 (1971); (b) D. J. Cram and L. Gosser, *ibid.*, **86**, 5445 (1964); (c) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 86–103.

(3) W. T. Ford, *J. Amer. Chem. Soc.*, **92**, 2857 (1970).

(4) H. Rapoport and G. Smolinski, *ibid.*, **82**, 934 (1960).

(5) (a) T. E. Hogen-Esch and J. Smid, *ibid.*, **87**, 669 (1965); (b) *ibid.*, **88**, 307 (1966).

(6) E. M. Kosower, *ibid.*, **80**, 3253 (1958).

(7) A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *ibid.*, **87**, 384 (1965).

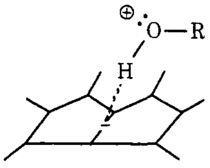
(8) The spectrum obtained in *n*-propylamine–THF (30 vol % *n*-$C_3H_7NH_2$) is identical with that in *n*-propylamine.

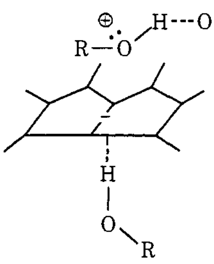
alcohol the new spectrum is fully developed (Figure 1). On addition of 1 equiv of the crown ether to this system, dramatic changes are observed in the spectrum. The rather broad bands in uv and visible regions narrow and red shift to give a separated ion-pair spectrum similar to that observed in aprotic media (Figure 1).

When these titrations are done with THF instead of THP, different phenomena are observed. The originally present bands corresponding to separated ion pairs (Table I) simply increase in intensity on addition of alcohol and no significant broadening or blue shift is apparent.

The above spectra can be most reasonably ascribed to ion pairs since calculated dielectric constants are low (<13) and because the changes observed on addition of crown ether to the THP-n-C_3H_7OH mixture cannot be explained on the basis of free anions.

Assuming that the broadened band near 380 nm in the THP-n-C_3H_7OH system is caused by H bonding, essentially two ion-pair structures can be envisioned,[10] I and II.


I


II

Similar structures were first proposed by Cram and Gosser[2b] in their work on the stereochemistry of substitution reactions at saturated hydrocarbon involving intermediate carbanions of a related type. On collapse of carbanion to hydrocarbon, I leads to retention and II to inversion of configuration. If II represents the structure of such an ion pair, its λ_{max} should be essentially unaffected by the state of coordination of the cation. The data show that this is not the case. It seems then that H bonding is promoted by cation and takes place "front side." Thus in the presence of powerful cation solvating ethers such as THF and particularly crown ether, the cation–alcohol coordination is disrupted and H bonding is essentially absent. The specificity of this phenomenon is especially obvious with the crown ethers since only 1 equiv is added per ion pair. Competitive H bonding to crown ether is, therefore, impossible owing to the very high alcohol concentration ($\simeq$3.5 *M*).

The spectroscopic results reported above provide reasonable evidence for H bonding and the role of cations in such bonding in the systems described above and are in substantive agreement with the stereochemical evidence in similar systems.[11]

Acknowledgments. Support by the Graduate School of the University of Florida and partial support by the National Science Foundation under Grant No. GH-34512 is gratefully acknowledged.

T. E. Hogen-Esch
Chemistry Department, University of Florida
Gainesville, Florida 32601

Received July 31, 1972

---

[9] Because of partial protonation of carbanion, an isosbestic point cannot be observed in the titration.

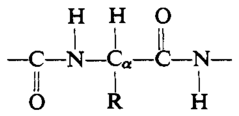
[10] Several alcohol molecules may actually be hydrogen bonding the carbanion.

[11] Roitman and Cram, in their studies on electrophilic substitution at saturated carbon involving carbanions as intermediates,[2a] observe racemization of asymmetric carbon and H–D exchange at about the same rate in the presence of equimolar quantities of base and crown ether, while in the absence of crown ether exchange with retention of configuration occurs. Other work on H–D exchange at asymmetric carbon[2b] involving ammonium carbanion salts as intermediates indicates exchange occurring with retention.[2b,c] It is interesting that in solvent systems where retention is observed the spectra of the FD⁻ ion pairs suggest front-side hydrogen bonding.

Conformational Dependence of Vicinal H–N–C–H Coupling Constants in Peptides

Sir:

Recent extensive applications[1–5] of vicinal H–N–C–H coupling are beginning to complement other types of investigations of polypeptide structures in solution. This technique makes use of some assumed mathematical relationship between the vicinal coupling constant and the dihedral angle ϕ measured about the N–C_α bond in the polypeptide backbone **1**.[6] In most cases



$$\begin{array}{ccccc} & H & H & O & \\ & | & | & \| & \\ -C- & N- & C_\alpha- & C- & N- \\ \| & & | & & | \\ O & & R & & H \end{array}$$

1

these relationships are of the form[1–4,9,10]

$$^3J_{HH'} = A\cos^2\theta + B\cos\theta + C \qquad (1)$$

which has been shown to provide an adequate representation of vicinal coupling in the H–C–C–H moiety.[11–14] In eq 1 θ is the dihedral angle measured

---

[1] V. F. Bystrov, S. L. Portnova, V. I. Tsetlin, V. T. Ivanov, and Y. A. Ovchinnikov, *Tetrahedron*, **25**, 493 (1969).

[2] W. A. Gibbons, G. Némethy, A. Stern, and L. C. Craig, *Proc. Nat. Acad. Sci. U. S.*, **67**, 239 (1970).

[3] (a) G. N. Ramachandran and R. Chandrasekaran, *Biopolymers*, **10**, 935 (1971); (b) G. N. Ramachandran, R. Chandrasekaran, and K. D. Kopple, *ibid.*, **10**, 2113 (1971).

[4] (a) A. E. Tonelli and F. A. Bovey, *Macromolecules*, **3**, 410 (1970); (b) A. E. Tonelli, A. I. Brewster, and F. A. Bovey, *ibid.*, **3**, 412 (1970); (c) A. E. Tonelli, *Proc. Nat. Acad. Sci. U. S.* **68**, 1203 (1971); (d) A. E. Tonelli, D. J. Patel, M. Goodman, F. Naider, H. Faulstich, and Th. Wieland, *Biochemistry*, **10**, 3211 (1971); (e) A. E. Tonelli, *J. Amer. Chem. Soc.*, **94**, 346 (1972); (f) A. E. Tonelli and A. I. Brewster, *ibid.*, **94**, 2851 (1972); (g) A. E. Tonelli, *Macromolecules*, **5**, 286 (1972).

[5] (a) R. J. Weinkam and E. C. Jorgensen, *J. Amer. Chem. Soc.*, **93**, 7038 (1971); (b) P. H. Von Dreele, A. I. Brewster, F. A. Bovey, H. A. Scheraga, M. F. Ferger, and V. du Vigneaud, *Proc. Nat. Acad. Sci. U. S.*, **68**, 3088 (1971); (c) D. A. Torchia, A. di Corato, S. C. K. Wong, C. M. Deber, and E. R. Blout, *J. Amer. Chem. Soc.*, **94**, 609 (1972); (d) D. A. Torchia, S. C. K. Wong, C. M. Deber, and E. R. Blout, *ibid.*, **94**, 616 (1972); (e) K. D. Kopple, A. Go, R. H. Logan, Jr., and J. Šavrda, *ibid.*, **94**, 973 (1972); (f) J. D. Glickson, D. F. Mayers, J. M. Settine, and D. W. Urry, *Biochemistry*, **11**, 477 (1972); (g) A. I. Brewster, J. A. Glasel, and V. J. Hruby, *Proc. Nat. Acad. U. S.*, **69**, 1470 (1972).

[6] Two different conventions for the specification of the angle ϕ are in common use.[7,8] The dihedral angle θ, which is used here, is related to these by $\theta = |\phi - 240^\circ|$[7] or $\theta = |\phi - 60^\circ|$.[8]

[7] J. T. Edsall, P. J. Flory, J. C. Kendrew, A. M. Liquori, G. Némethy, G. N. Ramachandran, and H. A. Scheraga, *Biopolymers*, **4**, 121 (1966).

[8] IUPAC–IUB Commission on Biochemical Nomenclature, *Biochemistry*, **9**, 3471 (1970).

[9] C. M. Thong, D. Canet, P. Granger, M. Marraud, and J. Néel, *C. R. Acad. Sci., Ser. C.*, **269**, 580 (1969).

[10] R. Schwyzer, private communication, quoted in footnote 24 of ref 5a.

[11] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

[12] M. Barfield and M. Karplus, *ibid.*, **91**, 1 (1969).

[13] M. Barfield and D. M. Grant, *Advan. Magn. Resonance*, **1**, 149 (1965).

[14] A. A. Bothner-By, *ibid.*, **1**, 195 (1965).