Proton Transfers in Dipolar Aprotic Solvents. V. Solvation and Geometric Factors in the Rates of Proton Transfer Reactions[1,2]

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Abstract: Data concerning the rates and equilibria of carbon acid–base reactions in methanol and dimethyl sulfoxide solutions are presented and interpreted to arrive at the following conclusions. (1) The pK's of carbon acids of the fluorene or triphenylmethane types are approximately 6 pK units lower in DMSO than in methanol solution. (2) The slow rates of proton transfers involving carbon acids are due to energy requirements for both solvent and internal geometric reorganizations on going from the acid to a resonance-stabilized conjugate base. (3) Internal geometric reorganizations contribute to the activation energies for fluorene-type acids, but not to oxygen acids because of extreme differences in the abilities of the two types of acids to hydrogen bond to the proton acceptor and thereby stabilize the transition states.

It is well known that carbon and oxygen acids of the same acid strength react with bases at markedly different rates.[3] Recently, Hine[4] has revitalized and extended the concept of the "principle of least action" and has shown how this concept can be used in a semiquantitative fashion to predict relative reactivities of various compounds in which reaction leads to changes in the geometries of the reacting molecules. Similar reasoning has been applied by Marcus[5] in the area of "outer sphere" electron-transfer reactions of inorganic species. Both Marcus' elaborate calculations and Hine's more qualitative treatments attribute a large fraction of the

activation energies for such reactions to the stretching or bending of bonds which occur on going from reactant to product.

It is clear, however, that the extent of geometric changes on going from reactant to product, alone, cannot explain the differences in the rates of reactions of carbon and oxygen acids. Table I contains data obtained from the literature which allow us to estimate closely the geometric changes involved in the ionizations of p-nitrophenol and of nitromethane. These estimates, and the sums of the squares of the bond length changes on ionization, are given in Table II. We see that these

Table I. Known Bond Lengths to be Used for the Estimation of Bond Length Changes on Ionizations

Compound	Bond	Length, A	Ref
CH_3NO_2	C–N	1.46	a
	N–O	1.21	
$O_2NCH_2CO_2K_2$	C–N	1.39	b
	N–O	1.27	
p-Nitroaniline	C–NO$_2$	1.41	c
	C–NH$_2$	1.37	
	N–O	1.27	
Nitrobenzene	C–N	1.49	d
	N–O	1.21	
p-Nitrophenol	C–N	1.44	e
	N–O	1.23	
	C–O	1.35	
o-Nitrophenoxide ion	C–N	1.39	f
	N–O	1.26	
	C–O	1.26	

a L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, p 113. *b* See footnote *a*, p 122. *c* See footnote *a*, p 199. *d* L. E. Sutton, Supplement, Special Publication No. 18, The Chemical Society, London, 1965. *e* See footnote *d*, p 18. *f* J. P. G. Richards, *Z. Krist.*, **116**, 468 (1961).

Table II. Estimated Bond Length Changes for the Ionizations of Nitromethane and of p-Nitrophenol

Bond	Molecule, A	Ion, Å	Change, Å
Nitromethane[a]			
C–N	1.46	1.39	0.07
N–O	1.21	1.27	0.06
p-Nitrophenol[a]			
C–N	1.44	1.38	0.06
N–O	1.23	1.28	0.05
C–O	1.35	1.26	0.09

a Sum of squares of bond length changes for nitromethane, 1.21×10^{-2} Å^2; for nitrophenol, 1.66×10^{-2} Å^2.

estimates would lead to the prediction that p-nitrophenol should react more slowly with a base than does nitromethane. From the considerations given by Marcus[5] and Hine,[4] the reactions that should be compared are the identity reactions in each case, *i.e.*, the rate of reaction of p-nitrophenol with p-nitrophenoxide ion, and the reaction of nitromethane with nitromethyl anion.

The first reaction, p-nitrophenol with p-nitrophenoxide ion, has been studied by nmr techniques.[6] At $-80°$ in methanol solution, the rate constant for the direct proton transfer is 4.3×10^6 M^{-1} sec^{-1}. The reaction of nitromethane with nitromethyl anion has not been studied. This reaction, however, is certainly slower than the reaction of nitroethane with methoxide ion, which has been studied.[7] At 25°, in methanol so-

(1) Previous paper in this series: C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **90**, 3415 (1968).

(2) The present paper should also be considered as paper VII in the series "Acidity in Nonaqueous Solvents." Previous paper: C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **90**, 2821 (1968).

(3) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959; see particularly p 13 ff, and Chapter X.

(4) J. Hine, *J. Org. Chem.*, **31**, 1236 (1966); *J. Am. Chem. Soc.*, **88**, 5525 (1966).

(5) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964), and earlier papers cited there.

(6) E. Grunwald, C. F. Jumper, and M. S. Puar, *J. Phys. Chem.*, **71**, 492 (1967).

(7) P. Jones, J. L. Longridge, and W. F. K. Wynne-Jones, *J. Chem. Soc.*, 3606 (1965).

lution, this latter reaction has a rate constant of 16.4 M^{-1} sec^{-1}. Thus, the identity reaction of nitrophenol is more than 10^5 faster than the corresponding reaction of nitromethane, in direct opposition to the prediction on the basis of geometric reorganization.

Although the data cited here have only recently become available, earlier data, enabling less direct comparisons, convinced us several years ago that factors other than the straightforward geometric changes were involved in the differences of behavior of carbon and oxygen acids. We have been carrying out work along several lines in an attempt to define the important factors in these differences.

Work already reported from our laboratories has established two important points. First, the proton transfer from methane to hydride ion in the gas phase is theoretically calculated to be quite similar to the analogous reactions of hydrogen fluoride, water, or ammonia.[8] From these calculations, we conclude that the differences in the behavior of the common carbon acids from other acids cannot be ascribed to some peculiar nature of carbon, or of the carbon–hydrogen bond. Second, we have found that there is a large increase in the rates of proton transfers from carbon acids, not attributable to an increased basicity of the proton acceptor, on going from hydroxylic to nonhydroxylic solvents.[1] We suggested that this effect is caused by a solvent reorientation in hydroxylic solvents which involves a reorganization or breaking of solvent–solvent hydrogen bonds on going from reactants to transition state for the carbon acids, but not for oxygen acids. This factor is visualized to be similar to that which we have previously suggested for the reactions of carbonium ions with nucleophiles,[9] and is thought to be associated with the "hydrophobic" solvation of the neutral carbon acids.

In the present paper, we report more data bearing on the solvent effect mentioned above, and present new data on rates and equilibria of carbon acid reactions in methanol and DMSO solutions. These new data provide confirmation of the general solvent effect on the acidities of fluorene and triphenylmethane-type acids which we previously suggested,[1,2] and, we believe, provides information on which a consistent explanation of the differences discussed above can be based.

Experimental Section

The preparations of most of the materials, and the description of the techniques, used in the present study have been presented in earlier papers.[1,2,9]

1,1,5,5-Bisbiphenylenepentadiene-1,4, compound I, was prepared as described by Kuhn, et al.[10] Melting point and spectral properties agreed closely with those reported.

9-Cyanofluorene was prepared by the procedure detailed by Wislicenus.[11]

Fluorenone oxime was prepared by the reaction of fluorenone with hydroxylamine and was recrystallized from methanol–water.

Tribenzylamine and n-butylamine were commercial products used without further purification.

The methoxyfluorenes were obtained from commercial sources and recrystallized from ethanol.

(8) C. D. Ritchie and H. F. King, J. Am. Chem. Soc., 90, 825, 833, 838 (1968).

(9) C. D. Ritchie, G. A. Skinner, and V. G. Badding, ibid., 89, 2063 (1967).

(10) R. Kuhn, H. Fischer, F. A. Neugebauer, and H. Fischer, Liebig's Ann., 654, 64 (1962).

(11) W. Wislicenus and K. Russ, Ber. Deut. Chem. Ges., 43, 2719 (1910).

tautomer Ia

tautomer Ib
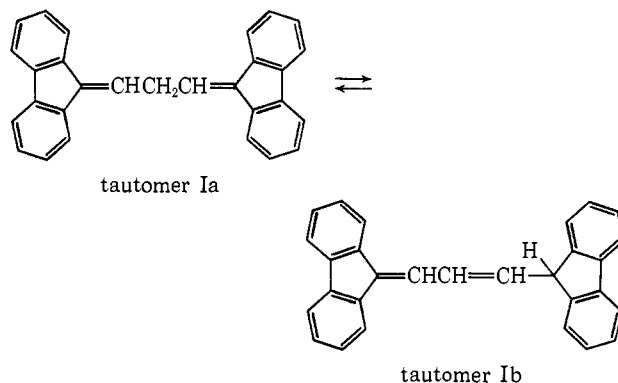
Results

The pK's and rate constants obtained in the present study are reported in Tables III and IV.

Table III. Acidities in DMSO and in Methanol

Compound	Solvent	pK	Lit. value
9-Cyanofluorene	DMSO	8.4	7.9–8.4[a]
1,1,5,5-Bisbiphenylene-pentadiene-1,4 (I)	DMSO	8.7	8.9[a]
Tautomer Ia	DMSO	8.1	
Tautomer Ib	DMSO	8.8	
9-Carbomethoxyfluorene	DMSO	10.3[c]	9.9[d]
Fluoradene	DMSO	10.5[c]	10.7[a]
9-Phenylfluorene	DMSO	16.4[c]	16.1[a] 17.0[e]
9-Methylfluorene	DMSO	19.7[c]	20.2[e]
4,5-Methylenephenanthrene	DMSO	20.0[c]	19.6[e]
4-Methoxyfluorene	DMSO	20.0	
Fluorene	DMSO	20.5[c]	20.5[e]
1-Methoxyfluorene	DMSO	20.8	
2-Methoxyfluorene	DMSO	21.1	20.8[e]
Tribenzylammonium ion	DMSO	4.1	
n-Butylammonium ion	DMSO	10.7	11.1[b]
9-Cyanofluorene	MeOH	14.2	
9-Carbomethoxyfluorene	MeOH	15.8	
Tribenzylammonium ion	MeOH	6.4[f]	
n-Butylammonium ion	MeOH		11.8[g]
Fluorenone oxime	DMSO	15.0	

[a] R. Kuhn and D. Rewicki [Liebig's Ann., 706, 250 (1967)] report pK values relative to tripropylammonium ion. The values given in this table are based on the assumption that tripropylammonium ion has the same pK in DMSO as does tributylammonium ion (8.4) which value has been reported by Kolthoff (see footnote b). [b] I. M. Kolthoff, M. K. Chantooni, and S. Bhowmik, J. Am. Chem. Soc., 90, 23 (1968). [c] Values previously reported from our laboratories; see ref 1. [d] K. Bowden and R. Stewart [Tetrahedron, 21, 261 (1965)] reported a value relative to 9-cyanofluorene in ethanol solution. The value given here is adjusted to the pK of 8.4 for 9-cyanofluorene. [e] K. Bowden and A. F. Cockerill, Chem. Commun., 989 (1967). Relative values of pK's in aqueous DMSO solutions were reported. The values given in this table are adjusted to the pK of 20.5 for fluorene. [f] Reference 9. [g] Reference 3.

Table III also compares the pK's of many of the compounds in DMSO solution to those which have been obtained on a relative scale by other workers. The agreement for the various hydrocarbons is much better than might have been expected considering the differences in solvent systems in several cases, and the variety of sources. We have previously commented on the reliability of the pK determinations by our technique, and estimate the accuracy of the values to be ±0.2 unit.

The pK determinations are based on the calibration of a glass electrode with dilute solutions of p-toluenesulfonic acid in DMSO. The reliability of the calibration

Table IV. Rates of Proton Transfer Reactions

Acid	Base	Solvent	$k_f{}^a$	Log $K_{eq}{}^b$
Compound I	p-Nitrobenzoate	DMSO	5.0×10^2	0.2
	p-Chlorobenzoate	DMSO	7.9×10^2	1.4
	p-Hydroxybenzoate	DMSO	4.8×10^3	3.1
	p-Aminobenzoate	DMSO	1.3×10^4	4.0
	p-Nitrophenoxide	DMSO	2.5×10^3	1.7
Fluoradene	p-Nitrophenoxide	DMSO	1.5×10^5	0.0
9-Cyanofluorene	p-Nitrobenzoate	DMSO	4.0×10^5	0.5
9-Cyanofluorene	Fluoradenyl ion	DMSO	8.2×10^3	2.1
9-CO_2CH_3-fluorene	Fluoradenyl ion	DMSO	1.0×10^3	0.2
9-Cyanofluorene	9-CO_2CH_3-fluorenyl ion	DMSO	3.3×10^3	1.9
9-CO_2CH_3-fluorene	n-Butylamine	DMSO	1.5×10^4	0.4
Fluoradene	n-Butylamine	DMSO	1.2×10^4	0.2
9-CO_2CH_3-fluorene	Methoxide ion	MeOH (4°)	2.4×10^3	2.6

^{a} Rate constants in units of M^{-1} sec^{-1} at 25° unless specified. ^{b} The logarithm of the equilibrium constant for the acid–base reaction.

has been confirmed by comparison of the values determined for the pK's of acids that have been studied by other techniques, particularly with values obtained on relative scales by indicator methods.[2] In the present work, we have been able to obtain further confirmation of the reliability of the calibration. Tribenzylammonium ion has a pK which allows the application of the differential potentiometric method.[12] The pK determined by this technique was in near-perfect agreement with the value determined with the calibration data.

The pK determination of 1,1,5,5-bisbiphenylenepentadiene-1,4 gives a gross value since the compound exists in two tautomeric forms in DMSO solution. The two forms are shown by structures Ia and Ib. Kuhn[13] has reported the tautomeric equilibrium constant in DMSO solution as 5, favoring the tautomer Ib. This value, along with the gross pK value of 8.7, gives the pK values of the two tautomers as shown in Table III.

The rate constants reported in Table IV were obtained by stop-flow techniques[1] under pseudo-first-order conditions. At least two different runs were made for each reaction using different concentrations of base to verify that second-order kinetics were obeyed. The rate constants were reproducible to better than 10%.

The rate of reaction of compound I was determined by following the appearance of the carbanion under pseudo-first-order conditions. The reactions showed very good first-order behavior and no differences in the rates of reactions of the two tautomers could be detected.

We also attempted to determine the rate of reaction of p-nitrophenol with benzoate ion in DMSO solution. The reaction was complete on mixing, and we can only set a lower limit of 5×10^6 M^{-1} sec^{-1} on the rate constant. In all probability, the reaction is diffusion controlled with a rate constant around 10^9–10^{10} M^{-1} sec^{-1}.

The pK measurements of 9-cyanofluorene and 9-carbomethoxyfluorene in methanol solution were performed by spectrophotometrically determining the amount of carbanion present in given concentrations of potassium methoxide. The procedure used is the same as that which we previously described for the determination of the pK of triphenylmethane in DMSO solution.[14]

(12) E. Grunwald, J. Am. Chem. Soc., **73**, 4934 (1951).
(13) R. Kuhn and D. Rewicki, Tetrahedron Lett., **39**, 3513 (1965).
(14) C. D. Ritchie and R. E. Uschold, J. Am. Chem. Soc., **89**, 2960 (1967).

Discussion

In this section, first we will discuss the changes in pK's of various acids on going from methanol to DMSO solution, second, the rate constants in DMSO and the changes in rates with change in solvent, and finally, we will relate the two previous discussions and suggest a consistent explanation for the differences in the behavior of carbon and oxygen acids in general.

Table V contains a wide range of data concerning the changes in pK's of various acids on going from meth-

Table V. pK's of Acids in DMSO and in Methanol Solutions

Acid	pK_{DMSO}	pK_{MeOH}	ΔpK^a
Ammonium ions			
$NH_4{}^+$	10.5^b	10.8^c	0.3
n-Butylammonium	10.7^d	11.8^c	1.1
Triethylammonium	9.0^b	10.9^c	1.9
Tribenzylammonium	4.1^d	6.4^d	2.3
Phenols			
2,6-Dinitrophenol	4.9^b	7.8^e	2.9
p-Nitrophenol	10.4^f	11.2^f	0.8
Phenol	16.4^f	14.2^c	-2.2
Carboxylic acids			
p-Nitrobenzoic	8.9^f	8.4^g	-0.5
p-Chlorobenzoic	10.1^f	9.1^g	-1.0
Benzoic	11.0^f	9.4^g	-1.6
m-Toluic	11.0^f	9.5^g	-1.5
m-Hydroxybenzoic	11.5^f	9.8^g	-1.7
p-Ethoxybenzoic	11.5^f	9.8^g	-1.7
Acetic	11.6^f	9.7^c	-1.9
Bicyclo[2.2.2]octane-1-carboxylic acid	12.5^f	10.2^f	-2.3
Hydrocarbons			
9-Cyanofluorene	8.4^d	14.2^d	5.8
9-Carbomethoxyfluorene	10.3^d	15.8^d	5.5
Fluoradene	10.5^f	17^f	6^b

^{a} ΔpK = pK_{MeOH} − pK_{DMSO}. ^{b} I. M. Kolthoff, M. K. Chantooni, and S. Bhowmik, J. Am. Chem. Soc., **90**, 23 (1968). ^{c} Reference 3. ^{d} Values reported in Table III. ^{e} B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, J. Am. Chem. Soc., **88**, 1911 (1966). ^{f} Data previously reported from these laboratories; see ref 1, 2, and 9. ^{g} J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, p 268.

anol to DMSO solution. The most outstanding feature of these data is the fact that the hydrocarbon acids behave in a manner quite different from any of the other types shown.

In the previous paper of this series,[2] we showed that the pK of fluoradene is at least six units greater in methanol than in DMSO solution. We postulated there

that other acids of the fluorene and triphenylmethane types would show similar changes on going from DMSO to methanol, and showed that kinetic data on the isotopic exchange of triphenylmethane in methanol could be easily interpreted with this postulate. The present results for the changes in pK's of 9-cyanofluorene and of 9-carbomethoxyfluorene fully confirm that postulate. The small differences in the pK changes observed (ca. 6.5 for fluoradene, 5.8 for 9-cyanofluorene, and 5.5 for 9-carbomethoxyfluorene) appear to be due to differences in the activity coefficients for transfer of the neutral fluorenes. Preliminary experiments indicate that the log of the activity coefficient for transfer of 9-carbomethoxyfluorene from methanol to DMSO is about 0.6 unit more negative than that for fluorene, triphenylmethane, or 9-phenylfluorene.[15]

If we attribute the decrease in ionization of benzoic acids on going from methanol to DMSO to hydrogen bonding of methanol to the benzoate ions, then it is obvious that we must conclude that the carbanions are far less importantly hydrogen bonded than are the benzoate ions. Comparison of the hydrocarbon acids to phenols leads to the conclusion that the carbanions are even less importantly hydrogen bonded in methanol than are the phenoxide ions such as 2,6-dinitrophenoxide ion. These qualitative conclusions are further strengthened by any attempt to evaluate single ion activities.

The change in pK on change of solvent is broken into the various contributing factors by

$$pK_{\mathrm{DMSO}} - pK_{\mathrm{MeOH}} = -\Delta pK =$$
$$+ \log \gamma_{\mathrm{H^+}} + \log \gamma_{\mathrm{A^-}} - \log \gamma_{\mathrm{HA}} \quad (1)$$

where the γ's are the "degenerate activity coefficients" for transfer of the subscripted species from methanol to DMSO solution. In the case of ammonium ions, of course, log $\gamma_{\mathrm{R_3N}}$ and log $\gamma_{\mathrm{R_3NH^+}}$ take the place of log $\gamma_{\mathrm{A^-}}$ and log γ_{HA}, respectively. The activity coefficients are related to the free energies of transfer of the ionic species by eq 2.

$$RT \ln \gamma_{\mathrm{HA}} = \Delta G^\circ_{\mathrm{t}} \text{ for the process}$$
$$(\mathrm{HA})_{\mathrm{MeOH}} \rightleftharpoons (\mathrm{HA})_{\mathrm{DMSO}} \quad (2)$$

For the neutral molecules, the activity coefficients can be directly determined by distribution experiments. Our preliminary results[15] indicate that the following values for the various type acids are approximately valid

$$\log \gamma_{\mathrm{RCOOH}} \cong -0.6$$
$$\log \gamma_{\mathrm{R_3N}} \cong -0.05 \quad (3)$$
$$\log \gamma_{\mathrm{HC}} \cong -0.5$$

Taking approximate values of ΔpK for the acid types, $\Delta pK_{\mathrm{RCOOH}} = 1.8$; $\Delta pK_{\mathrm{R_3NH^+}} = 2.0$; and $\Delta pK_{\mathrm{HC}} = 6.0$, we obtain the following approximate values for sums and differences of ionic activity coefficients

$$\log \gamma_{\mathrm{H^+}} + \log \gamma_{\mathrm{RCOO^-}} \cong 1.2$$
$$\log \gamma_{\mathrm{H^+}} + \log \gamma_{\mathrm{C^-}} \cong -6.5$$
$$\log \gamma_{\mathrm{H^+}} + \log \gamma_{\mathrm{R_3NH^+}} \cong -2.0$$
$$\log \gamma_{\mathrm{RCOO^-}} - \log \gamma_{\mathrm{C^-}} \cong 7.7 \quad (4)$$
$$\log \gamma_{\mathrm{C^-}} + \log \gamma_{\mathrm{R_3NH^+}} \cong -4.5$$
$$\log \gamma_{\mathrm{RCOO^-}} + \log \gamma_{\mathrm{R_3NH^+}} \cong 3.2$$

(15) Preliminary results of unpublished work in our laboratories by B. M. McKay.

These equations, particularly the last three, clearly indicate the "abnormal" behavior of the carbanions relative to carboxylate ions or ammonium ions. We emphasize again the conclusion that carbanions and carboxylate ions are quite markedly different with respect to hydrogen bonding in methanol solution.

In order to go beyond these results, we must introduce a value for at least one of the single ion activity coefficients. Parker[16] has recently summarized the various attempts at the evaluation of single ion activity coefficients for transfer from methanol to dipolar aprotic solvents. Although all of the approaches are open to criticisms, entirely different approaches give approximately the same result. There is, therefore, some justification for the assignment of these values in that they are self-consistent. The most pertinent value for the present purposes is that for the transfer of acetate ion from methanol to DMSO solution. The value of log $\gamma_{\mathrm{RCOO^-}}$ is given as 6.5. Using this value, we find

$$\log \gamma_{\mathrm{C^-}} = -1.2$$
$$\log \gamma_{\mathrm{R_3NH^+}} = -3.3 \quad (5)$$
$$\log \gamma_{\mathrm{H^+}} = -5.3$$

The negative value for the free energy of transfer of the proton from methanol to DMSO is consistent with the known relative basicities of the two solvents,[17] and the relative values for the proton and the trialkylammonium ion are reasonable in terms of the expected relative abilities of the species to hydrogen bond to the more basic DMSO solvent.

The negative free energy for transfer of the carbanion from methanol to DMSO solution is most reasonably ascribed to the greater polarizability of DMSO[1,2] leading to strong interactions with the highly polarizable carbanions.[18] Since these polarization energies are expected to differ among solvents by only a few kilocalories, at most,[18] however, we must conclude that the hydrogen bonding of methanol to the carbanions is extremely weak, and perhaps nonexistent.

We suggest that the presence of a localized lone pair of electrons is a necessary requisite for important hydrogen bond accepting properties.[19] Thus, even though o- or p-nitro-substituted phenoxides have delocalization of the negative charge, there are still other lone pairs available on oxygen for hydrogen bonding, and the phenoxides are strongly stabilized in methanol solution. The different behaviors of hydrocarbons and amines on ionization in aqueous DMSO solvents[20] are also understandable on this basis.

Turning now to the rates of proton transfer reactions involving the hydrocarbon acids, we would first like to focus attention on the solvent effect which we previously discussed.[1] In the previous paper, we compared the reactions of fluoradene and of 9-carbomethoxyfluorene with benzoate ions in DMSO to the isotope exchange reactions of various fluorenes in methanol solution. In the present work, we have been able to measure di-

(16) A. J. Parker, et al., J. Am. Chem. Soc., 90, 5049 (1968), and earlier papers cited there.
(17) E. M. Arnett, Prog. Phys. Org. Chem., 1, 233 (1963).
(18) E. Grunwald and E. Price, J. Am. Chem. Soc., 86, 4517 (1964).
(19) The suggestion that delocalized lone pairs are not good hydrogen bond acceptors was made by Bunton and Shiner in one of the basic rules for the estimation of solvent isotope effects: C. A. Bunton and V. J. Shiner, ibid., 83, 42 (1961).
(20) C. D. Ritchie and R. E. Uschold, ibid., 89, 2752 (1967).

rectly the rate of reaction of methoxide ion with 9-carbomethoxyfluorene in methanol solution. Moreover, the pK value determined for the hydrocarbon in methanol allows us to evaluate the equilibrium constant for the reaction of methoxide ion. If this point is then placed on a Brønsted plot of the previous data for DMSO solution, it falls approximately two units below the correlation line. This more direct comparison than the previously given one[1] supports the conclusions concerning the solvent effect on these acid–base reactions: there is a solvent effect on the rates, not ascribable to changes in the solvation of the base, which accounts for a factor of ca. 10^2 on going from methanol to DMSO solution. We believe that this effect is a solvent reorientation effect in methanol solution, and probably in other hydroxylic solvents, which arises from the differences in solvation of the carbon acid and its conjugate base. We have discussed this factor in earlier papers.[1,2,9]

It is quite apparent from the data that factors other than solvent reorientation are also important in contributing to the slowness of the carbon acid reactions. The rate constants shown in Table IV for compound I are considerably lower than those previously reported for 9-cyanofluorene and 9-carbomethoxyfluorene with the base in the same solvent. The amount of geometric rearrangement in compound I on ionization is much greater than for 9-substituted fluorenes, and the indication is strong, then, that geometric rearrangement contributes to the energies of activation.

The reactions of fluorenyl anions with fluorenes, reported in Table IV and in the earlier paper,[1] obey the Brønsted relationship fairly well. The slope of the correlation is close to 0.5; $\log k_0{}^{21}$ is ca. 3. Only the reaction of 9-phenylfluorene with 9-methylfluorenyl anion falls appreciably off the correlation line, probably as a result of steric effects. This correlation line, however, is ca. 10^2 below the line defined by the reactions of fluoradene or 9-carbomethoxyfluorene with benzoates, and is near the line for reactions of compound I with benzoates ($\log k_0{}^{21} = 2.6$). Both of these observations are consistent with the expectations on the basis of geometric rearrangements during the reactions.

Our data, then, indicate that carbon acids are slow in proton transfer reactions due to two factors: internal geometric rearrangements on ionization to which the principle of least action[4] is applicable, and a solvent reorientation in hydroxylic solvents. As we have discussed,[1,2,9] it is understandable that solvent reorientation is a factor for carbon, but not oxygen, acids because of known differences in the solvation of these species. It is not as easy to understand why the carbon acids are subject to contributions to activation energies from geometric rearrangements while the oxygen acids are not.

(21) k_0 refers to the rate constant for the (hypothetical) acid–base reaction having an equilibrium constant of unity.

We believe that the solvent effects on pK's discussed above provide a basis for the understanding of this latter point. Both Hine[4] and Marcus[5] have emphasized that their ideas rest on the assumption of weak interactions between the reacting partners at the transition state. Any strong interaction between the partners could provide enough energy to accomplish the geometric changes. In an acid–base reaction, the most likely source of strong interaction is hydrogen bonding. We suggest that the same weakness of hydrogen-bonding capability of carbanions that manifests itself in the solvent effects on acidities discussed above is also responsible for weak interactions of carbanions with acids, or of hydrocarbons with bases, in the transition states for the proton transfers, thus forcing energy input for the geometric changes on going from reactant to transition state. In the reactions of oxygen acids and bases, the hydrogen bonding is generally strong enough to provide the energy for geometric changes on going to the transition states.

The ideas offered above lead to a number of predictions which might be checked by further experiments. First, those carbon acids whose conjugate bases have a localized charge are predicted to have proton transfer rates considerably greater than acids of the same thermodynamic strength whose conjugate bases have delocalized charges. That is, saturated hydrocarbons, alkenes, alkynes, and cycloalkanes whose conjugate bases are localized are expected to show "kinetic acidities" greater than their thermodynamic acidities. We stongly suspect that Cram's MSAD[22] scale, and Streitwieser's isotope exchange studies,[23] seriously underestimate the pK's of such compounds.

Second, the generalization that nitrogen acids and bases react at diffusion-controlled rates is expected to be subject to the qualification that the lone pair on the nitrogen must be localized. In cases where this pair is delocalized, we expect proton transfers to occur at rates comparable to those of the corresponding carbon system. We are currently pursuing experiments dealing with this point.

(22) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 19.
(23) A. Streitwieser, et al., J. Am. Chem. Soc., **90**, 644, 648 (1968); **91**, 527, 529 (1969). See also ref 21, p 18.