supported by the fact that no polymer is obtained in the photolysis of phenyl azide sensitized by acetophenone (items marked with *b* in Table I), where the nitrene must be in the triplet state. Assuming then that the polymer is an insertion product of singlet nitrene, that aniline is a product of the nitrene triplet, and that azobenzene is not specific for either species, it may be concluded that in the photolysis of phenyl azide at least 50%, but possibly up to 95%, of the nitrene is produced in the singlet state.

The large margin of uncertainty in this estimate is due to the presence of azobenzene in the products. This difficulty can be overcome by using alcohols as substrates. Photolysis of phenyl azide in methanol and in 2-propanol produces little azobenzene, only small amounts of aniline, no polymer, and a major product which is unstable on the chromatographic plates and turns rapidly into several colored compounds and formanilide. This product is not found in the sensitized photolysis (acetophenone) of phenyl azide in alcohols and is also absent in the direct photolysis of phenyl azide in *tert*-butyl alcohol; it is therefore thought to arise by insertion of the nitrene singlet into the α-CH bond of the alcohol.

A series of experiments in alcohol–hydrocarbon mixtures was carried out. The results obtained in the system benzene–methanol are shown in Figure 1.

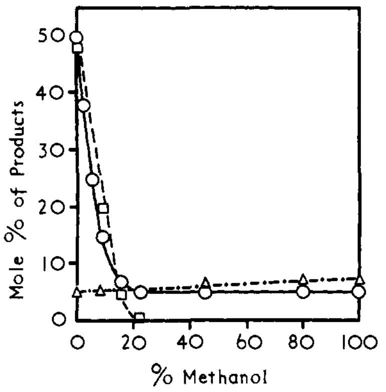

Figure 1. Effect of solvent composition on product yield in the direct photolysis of phenyl azide in benzene–methanol mixtures: ○, azobenzene; □, polymer; △, aniline.

With increasing alcohol content, the yield of azobenzene decreases rapidly to a limiting value of 5%, the polymer disappears altogether, and the yield of aniline remains virtually unchanged. This indicates that in pure methanol all singlet nitrenes have been intercepted, and that under these conditions both azobenzene and aniline are products of triplet nitrene. Similar results were obtained with isopropyl alcohol as solvent.

It is concluded that in the photolysis of phenyl azide the nitrenes appear predominantly in the excited singlet state and only 12–13% are generated directly in the triplet ground state.

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Received April 28, 1971

Hydrogen Bonding.[1] VI. A Dramatic Difference between Proton Transfer and Hydrogen Bonding

Sir:

A number of years ago, Gordy and Stanford[2] reported for a variety of compounds a good correlation between their ability to accept protons from aqueous acid (pK_a) and their hydrogen-bonding acceptor ability, as represented by their effect on the O–D stretching frequency of deuteriomethanol. In the ensuing years many authors[3] have implied that hydrogen bonding and proton transfer could be used almost interchangeably as measures of the same property—"basicity." Work cited here and reported below indicates that important differences in these properties may arise. In previous papers in this series[4] we have developed with our collaborators (Taft and Schleyer) a variety of methods for determining thermodynamic properties for hydrogen bonding using *p*-fluorophenol, PFP, in carbon tetrachloride as solvent at 25°. These methods give results which are not only self-consistent (usually within 0.1 kcal), but which also agree with the best data from other laboratories. We have also demonstrated the failure of the Badger–Bauer relation to correlate $\Delta\nu$ with heats of hydrogen bonding, ΔH_f, for some compounds.[4a] Neither is there a general correlation of $\Delta\nu$ with the free energy of hydrogen bond formation. In another series of papers[5] we have developed the use of ΔH_i, the heat of transfer from carbon tetrachloride (or some other inert solvent), to high dilution in fluorosulfuric acid at 25° as a useful criterion of Brønsted basicity. This criterion has the advantage over pK_a that all measurements are made under the same conditions in the same medium by the same method, thereby avoiding many of the difficulties which surround determination of the pK_a's of weak bases through the Hammett acidity function method.[6] Figure 1, therefore,

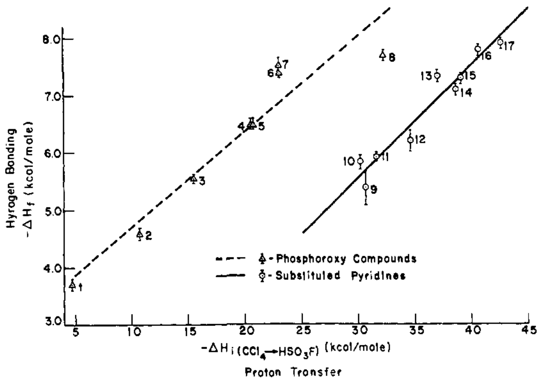

Figure 1. Relationships between hydrogen bonding and proton transfer for the compounds in Table I.

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[1] Supported by NSF Grant No. GP-6550-X and in part by the Office of Saline Water.

[2] W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **9**, 204 (1941).

[3] See, however, W. Tamres, S. Searles, E. M. Leighly, and D. M. Mohrman, *J. Amer. Chem. Soc.*, **76**, 3983 (1954).

[4] (a) E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie, and P. v. R. Schleyer, *ibid.*, **92**, 2365 (1970); (b) D. Gurka and R. W. Taft, *ibid.*, **91**, 4794 (1969); (c) R. W. Taft, D. Gurka, L. Joris, P. v. R. Schleyer, and J. W. Rakshys, *ibid.*, **91**, 4801 (1969).

[5] (a) E. M. Arnett, R. P. Quirk, and J. J. Burke, *ibid.*, **92**, 1260 (1970); (b) E. M. Arnett, R. P. Quirk, and J. W. Larsen, *ibid.*, **92**, 3977 (1970).

[6] E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

Table I. Thermodynamics of Protonation and Hydrogen Bonding for Substituted Pyridines and Phosphoroxy Compounds

Compound	$\Delta \overline{H}_{s(CCl_4)}$, kcal/mol	$-\Delta \overline{H}_{s(HSO_3F)}$, kcal/mol	$-\Delta H_f$,[a] kcal/mol	$-\Delta H_f$,[b] kcal/mol
(1) Phosphoroxy chloride	+0.39 ± 0.03	4.4 ± 0.1	3.71 ± 0.08	
(2) Dichlorophenylphosphine oxide	+0.84 ± 0.03	9.9 ± 0.3	4.59 ± 0.08	
(3) Diethyl chlorophosphate	+0.77 ± 0.02	14.7 ± 0.3	5.55 ± 0.07	
(4) Trimethyl phosphate	+0.76 ± 0.03	19.6 ± 0.1	6.44 ± 0.09	6.5 ± 0.1
(5) Triethyl phosphate	+0.02 ± 0.05	20.6 ± 0.2	6.59 ± 0.09	6.5 ± 0.1
(6) Triphenylphosphine oxide	+4.15 ± 0.23[c]	18.8 ± 0.2[c]		7.4 ± 0.1[d]
(7) Diethyl ethylphosphonate	−0.64 ± 0.09	23.6 ± 0.3	7.46 ± 0.12	
(8) Trimethylphosphine oxide	+5.23 ± 0.09	27.0 ± 0.6		7.7 ± 0.2
(9) 3,5-Dichloropyridine	+4.28 ± 0.06	26.4 ± 0.3		5.4 ± 0.3
(10) 2-Bromopyridine	+0.96 ± 0.03	29.2 ± 0.3	5.83 ± 0.09	
(11) 2-Chloropyridine	+0.96 ± 0.04	30.7 ± 0.3	5.93 ± 0.07	
(12) 3-Bromopyridine	+0.23 ± 0.03[d]	34.4 ± 0.3[c]		6.2 ± 0.2[d]
(13) Quinoline	+0.46 ± 0.01[d]	36.5 ± 0.2	7.47 ± 0.09[d]	7.35 ± 0.1[d]
(14) Pyridine	+0.36 ± 0.02[d]	38.2 ± 0.2[c]	7.40 ± 0.09[d]	7.1 ± 0.1[d]
(15) 4-Methylpyridine	−0.05 ± 0.01[d]	39.1 ± 0.3	7.59 ± 0.08[d]	7.3 ± 0.1[d]
(16) 2,6-Dimethylpyridine	−0.26 ± 0.06	41.0 ± 0.2[c]	8.44 ± 0.11	7.8 ± 0.3
(17) 2,4,6-Trimethylpyridine	−0.23 ± 0.03	42.9 ± 0.2	8.36 ± 0.12	7.9 ± 0.1

[a] These values were determined using method II, described in ref 4a. [b] These values were determined using method I, described in ref 4a, and where available are the values plotted as $-\Delta H_f$ in Figure 1. Other data plotted in Figure 1 were determined by use of method II. [c] Reference 5a. [d] Reference 4a.

represents a test of the relationship between hydrogen bonding and proton transfer through two well-established thermodynamic procedures and so is probably on solid experimental ground.

The results listed in Table I and portrayed in Figure 1 may be interpreted in at least two ways: (1) that there is a fundamental difference in the way pyridines and phosphoroxy compounds respond as hydrogen bond acceptors in carbon tetrachloride and as proton acceptors in fluorosulfuric acid; and (2) alternatively, the difference between the two series could be assigned to specific differences in the ability of fluorosulfuric acid to solvate pyridinium as compared to phosphoroxonium ions.

Evidence against the second explanation comes from two sources, the first of which being an extensive survey of a number of different types of compounds which gave a close correlation between pK_a and ΔH_i in fluorosulfuric acid. Deviations from this correlation were generally less than 2 kcal/mol even though the correlation covered nearly 50 kcal/mol in terms of each thermodynamic property.[5a] It would require a discrepancy of nearly 15 kcal/mol in ΔH_i in order to superimpose the two correlation lines portrayed in Figure 1. This would seem to be an unreasonably large and specific solvation difference. Secondly, Taft has reported exactly the same type of dispersal of correlation lines for different functional groups in an attempted free energy correlation between the free energy of hydrogen bonding, H, and the pK_a's for the same compounds in water.[4c] Further evidence for the consistency of our data is provided by the fact that ΔH_f for most of the hydrogen bond acceptors shown in Figure 1 gave excellent agreement when determined by the two techniques reported in ref 4a; *i.e.*, formation of a 1:1 complex with PFP at high dilution in carbon tetrachloride or by the injection of solid PFP into the hydrogen bond acceptor serving both as base and solvent. If the two different types of compounds suffered drastically different medium effects in their hydrogen bond formation with PFP, we would expect it to show up in large differences between ΔH_f as determined by the two methods.

We conclude that there are not important differential solvation factors for different families in fluorosulfuric acid or carbon tetrachloride and accordingly that most of the dispersal shown in Figure 1 and in Taft's work[4c,7] arises from different responses of different classes of bases to the two processes, proton transfer and hydrogen bonding. In view of the importance of acid catalysis and hydrogen bonding to phosphoroxy and heterocyclic bases, it is important to realize that various criteria of "basicity" may mean entirely different things in these two series of compounds and probably many others.

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(7) H. B. Yang and R. W. Taft, *J. Amer. Chem. Soc.*, **93**, 1310 (1971).

(8) NSF Trainee.

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Received May 24, 1971

Flash Photolysis of *N*-Chloroacetyl-*m*-tyramine

Sir:

A common feature of the mechanism underlying the novel photocyclization reactions of *N*-chloroacetylphenethylamines[1] appears to be homolytic or heterolytic cleavage of the C–Cl bond. On the basis of studies on fluorescence quenching[2] and solvent effects a dualistic mechanism has been proposed.[3] In water and protic solvents there is *intramolecular electron transfer* from the excited aromatic chromophore, while in most organic solvents *energy transfer* becomes intramolecular. In aqueous systems photoionization of the electron-donating aromatic nucleus[4] may precede electron scavenging by the chlorinated amide.[5]

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(1) O. Yonemitsu, Y. Okuno, Y. Kanaoka, and B. Witkop, *J. Amer. Chem. Soc.*, **92**, 5686 (1970); O. Yonemitsu, H. Nakai, Y. Kanaoka, I. L. Karle, and B. Witkop, *ibid.*, **92**, 5691 (1970).

(2) T. McCall, G. S. Hammond, O. Yonemitsu, and B. Witkop, *ibid.*, **92**, 6991 (1970).

(3) O. Yonemitsu, H. Nakai, Y. Okuno, S. Naruto, K. Hemmi, and B. Witkop, *Photochem. Photobiol.*, in press.

(4) (a) L. I. Grossweiner and H. I. Joschek, *Advan. Chem. Ser.*, **No. 50**, 279 (1965); (b) H. I. Joschek and L. I. Grossweiner, *J. Amer. Chem. Soc.*, **88**, 3261 (1966); (c) Yu. A. Vladimirov, D. I. Roshchupkin, and E. E. Fesenko, *Photochem. Photobiol.*, **11**, 227 (1970).

(5) P. B. Ayscough, R. G. Collins, and F. S. Dainton, *Nature (London)*, **205**, 965 (1965); A. Meybeck and J. J. Windle, *Photochem. Photobiol.*, **10**, 1 (1969).