

Thermometric Titrations of Substituted Pyridines with Trifluoroacetic Acid in Carbon Tetrachloride. Hydrogen Bonded Ion Pair Systems

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Abstract: A novel thermometric titration method is described in which acid and base solutions are pumped simultaneously into a large volume of solvent. This allows the maintenance of a constant stoichiometric relationship between the two reactants. The technique investigates the enthalpies for reaction of equal amounts of acid and base ($\Delta H_{1,1}$) and for the stoichiometries of 2:1 base to acid ($\Delta H_{2,1}$) and 2:1 acid to base ($\Delta H_{1,2}$). The bases are a series of pyridines and the acid is trifluoroacetic acid. Strict proportionality is found between the effects of substituents on $\Delta H_{1,1}$, $\Delta H_{1,2}$, and $\Delta H_{2,1}$. The results can be rationalized in terms of complete or partial formation of the ion pairs corresponding to the three stoichiometries, i.e., $BH^+—A^-$, $BH^+—AHA^-$, and $BH^+—BA^-$. The cases of 2,6-di-*tert*-butylpyridine and "Proton Sponge" are discussed in some detail.

Introduction

Brønsted acid-base interactions in nonbasic, nonpolar solvents have been discussed in the classic monograph of Davis¹ and several other reviews.²⁻⁷ These tell us that such systems must involve a bewildering array of hydrogen bonded complexes between the neutral species and between the ion pairs produced by protolysis. The structures of these complexes are easy to postulate but often difficult to demonstrate. This situation is analogous to that of acid-base systems in water, or other good dissociating media, where ion-pairing interactions are replaced by a multitude of ion-solvent interactions whose structures may be ambiguous and controversial. In both cases, structures in the crystalline state may be cited as prototypes but their actual relation to structures in solution often remains vague.

The pioneering work of Barrow and his co-workers⁸⁻¹⁴ attacked the nature of hydrogen bonded ion pair systems in nonpolar media by infrared spectroscopy and much of the subsequent literature has been cited by DeTar and Novak¹⁵ and Dega-Szafran, Grech, Naskret-Barciszewska, and Szafran.¹⁶ We shall refer to only the most relevant contributions here. This spectroscopic work is supported by studies of conductance, colligative properties, dielectric polarization, and several other experimental techniques¹ in specifying several types of structures which may be in equilibrium with each other and with the monomeric acid (HA) and base (B) over different parts of the normal concentration range of solution studies (10^{-1} – 10^{-6} M). The simplest and most clearly defined of these species are acid dimers (HA)₂,¹⁷ the 1:1 hydrogen bonded complex between acid and base B—HA, the 1:2 hydrogen bonded complex between base and acid dimer (B—HA—HA), 1:1 hydrogen bonded ion pairs between the conjugates of the original acid-base pair ($BH^+—A^-$), the 1:2 homoconjugate¹ ion pair complex ($BH^+—A^-—HA$) involving two molecules of acid, and the 2:1 homoconjugate ion pair involving two molecules of base ($B—H^+—BA^-$). Striking evidence for the role of hydrogen bonding between these ions is shown by the systematic differences which may be demonstrated between the behavior of quaternary ammonium salts in contrast to those derived from primary, secondary, or tertiary ammonium ions.¹ It follows that the behavior of homoconjugate ion pairs from tertiary amines ($BH^+—BA^-$) should be simpler than from secondary or primary ions because the latter ($BH_2^+—BHA^-$ and $BH_3^+—BH_2A^-$) have more sites available for the formation of higher aggregates such as (HB—HB⁺H—A⁻) or (HB—H—B⁺—H—B—H—A⁻).

Strong evidence may be cited also for the presence of higher

aggregates with stoichiometries equivalent to the above species¹⁶ and some of our results presented here support this inference.

It is worth noting that an added question in the understanding of such systems is how clearly differentiated such species may be in terms of their characterization as "single-minimum" and "double-minimum" hydrogen bonded species.^{15,18,19}

Thermometric titration²⁰⁻²⁵ is a powerful tool for acid-base study. However, its application to the titration of amines in nonpolar media has been largely ignored since the original work of Hume's group²⁶⁻²⁹ and Mead.³⁰ The only deliberate study of ion pairs by this method known to us is that of Gol'dshtein, Gur'yanova, and Perepelkova.³¹

In this article we will report the enthalpimetric titration of a series of substituted pyridines with trifluoroacetic acid (TFA) in CCl₄ at 25 °C. A novel double buret method is used which maintains the stoichiometries of acid and base constant during the titration. In this manner we have investigated the enthalpies of reaction of these bases with TFA at stoichiometries corresponding to formation of the 1:1 ($BH^+—A^-$) complex, the 1:2 (BH^+AHA^-) complex, and the 2:1 (BH^+BA^-) complex.

Experimental Section

Heats of reaction of substituted pyridines with TFA in CCl₄ at 25 °C were measured with a Tronac 450 titration calorimeter^{24,25} which was modified (Figure 1) by the addition of a second micrometer syringe (2.00 mL) which could be emptied or filled mechanically by a Hurst Model ARDA, 4 rpm synchronous motor. The design of the calorimeter permits both the motor-driven burets and the reaction vessel to be submerged completely inside the constant-temperature (25.000 ± 0.001 °C) bath. The rates of delivery of both burets were calibrated by weighing samples of water expelled during different periods of time and were identical as 0.395 ± 0.001 mL/min. Other details have been presented elsewhere.³²

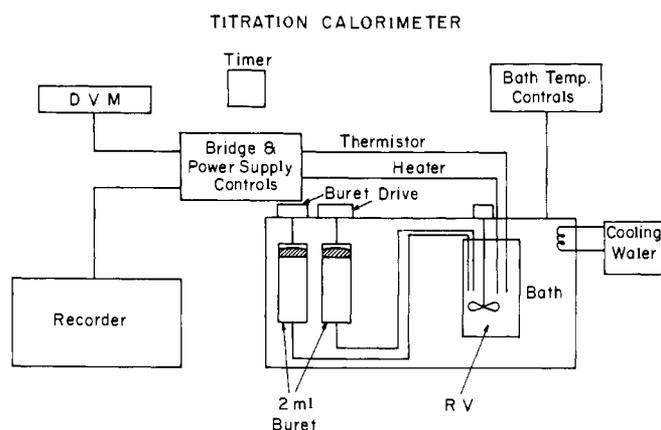
The solutions of pyridines and TFA were prepared by weighing the desired amount of solute into a 50-mL volumetric flask inside an argon-filled drybox (Kewaunee Scientific Equipment) and were subsequently diluted with solvent (CCl₄) using a syringe through a septum cap.

The motor-driven burets were filled with the two solutions by drawing samples through the syringe needles under dry argon. An air space of about 0.5 in. was left at the tip of each buret delivery tube to prevent premature reaction. The calorimeter vessel was cleaned, dried, and capped with a rubber septum after flushing with dry argon for about 0.5 h. It was then filled with 40 mL of dry CCl₄ from a 50-mL syringe and connected to the calorimeter insert assembly. A dry argon atmosphere was maintained at the top of the reaction vessel to protect the solvent from air. Next the calorimeter assembly, including the

Table I. Titration of Various Substituted Pyridines with Trifluoroacetic Acid in Carbon Tetrachloride at 25 °C

Base	$-\Delta H_{1,1}$	$-\Delta H_{1,2}$ kcal mol ⁻¹ ^a	$-\Delta H_{2,1}$
1. 3,5-Dichloropyridine	2.14 ± 0.10	4.35 ± 0.15	2.35 ± 0.10
2. 2-Chloropyridine	4.38 ± 0.11	5.01 ± 0.15	4.76 ± 0.11
3. 3-Bromopyridine	5.25 ± 0.11	7.98 ± 0.16	6.12 ± 0.12
4. 2,6-Di- <i>tert</i> -butylpyridine	4.40 ± 0.11	6.81 ± 0.16	4.98 ± 0.11
5. Pyridine	8.97 ± 0.10	14.90 ± 0.16	9.27 ± 0.14
6. 4-Methylpyridine	9.45 ± 0.13	16.03 ± 0.21	9.27 ± 0.13
7. 3,5-Dimethylpyridine	9.23 ± 0.13	15.27 ± 0.22	8.99 ± 0.13
8. 4-Methoxypyridine	10.28 ± 0.14	16.83 ± 0.22	10.57 ± 0.15
9. 2,4,6-Trimethylpyridine	11.39 ± 0.15	19.06 ± 0.23	11.80 ± 0.15
10. 1,8-Bis(dimethylamino)naphthalene	13.88 ± 0.17	23.41 ± 0.27	15.28 ± 0.18

^a These enthalpies are calculated on the basis of moles of the pyridine. These are observed values at the stoichiometries which are shown. Since the reactions may not be quantitative, these are not necessarily true thermodynamic enthalpies of formation of the complexes with the stoichiometries shown at the head of the column (see Discussion).

**Figure 1.** Schematic of double-buret thermometric titration assembly.

burets, was lowered into the constant-temperature bath and allowed to stand for 20–30 min until thermal equilibrium was reached.

The titrations were performed by simultaneously adding 1–2 mL of the two solutions of pyridine and of TFA at the same rate of delivery. In this manner constant stoichiometric acid:base ratios could be maintained throughout a run. Control experiments for corrections due to heat of dilution were run separately.

The commercially available liquid pyridines were distilled over solid KOH and stored overnight over activated molecular sieves. 3,5-Dichloropyridine was recrystallized from water and dried in a vacuum oven for 12–20 h. Trifluoroacetic acid (Matheson Coleman and Bell) was refluxed over P₂O₅ for 12 h and distilled. It was stored in an argon-filled drybox in a stoppered bottle. The purity of the compounds was established by melting point, boiling points, and gas chromatography.

A commercial (Aldrich) sample of 1,8-bis(dimethylamino)naphthalene (Proton Sponge) was recrystallized five or six times from ethanol until clean, white crystals were obtained. It was dried in a vacuum oven for about 8–10 h.

p-Anisidine (Aldrich Chemical Corp.) was recrystallized from distilled water (mp 57 °C). It was dried in a vacuum oven for 24 h and stored in the drybox.

Trichloroacetic acid (Fisher Certified Reagent) was dissolved in purified benzene and the benzene-water azeotrope distilled off. This was done twice, and then the acid was recrystallized from the remaining benzene solution. Manipulations were carried out under dry nitrogen. It was dried in the vacuum oven for about 40 h and stored in the drybox.

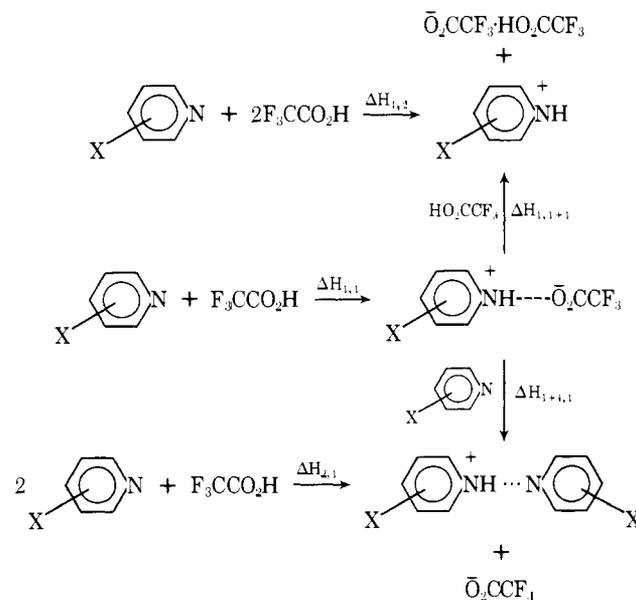
Thiophene-free benzene (Mallinckrodt Analytical Reagent) was refluxed over sodium metal, distilled, and stored over molecular sieves.

Carbon tetrachloride (Baker Analytical Reagent) was treated with a saturated solution of KOH in water for several hours to remove CS₂ and then washed with water. The CCl₄ was treated with concentrated H₂SO₄, then washed with water, dried over anhydrous CaCl₂, and distilled over P₂O₅. It was stored over activated molecular sieves. The

solvent purified in this way was found to contain less than 0.002% of water by Karl Fischer titration.

Results

The molar enthalpies of reaction for the following processes were measured at 25 °C and are presented in Table I.



The concentration of pyridine and TFA in final solutions ranged from 2×10^{-3} to 6×10^{-3} M. The enthalpies of the above-mentioned reactions were calculated from the following heat terms and are converted into molar enthalpies based on pyridine.

$$Q_{n,m} = Q_{n,m}^{\text{reaction}} - Q_{\text{py}}^{\text{dil}} - Q_{\text{TFA}}^{\text{dil}}$$

where $Q_{n,m}^{\text{reaction}}$ is the heat evolved when n moles of pyridine react with m moles of TFA (including heats of dilution of pyridine and TFA) in presence of CCl₄. $Q_{\text{py}}^{\text{dil}}$ is the heat evolved per n moles during the control experiment by the addition of 1–2 mL of pyridine solution to 40 mL of CCl₄ and $Q_{\text{TFA}}^{\text{dil}}$ is for TFA for m moles, for similar experiment.

The validity of the two-buret method was checked against the one-buret method by measuring the heat of protonation of an aqueous solution of Tham [tris(hydroxymethyl)amino-methane] with aqueous hydrochloride solution. Our ΔH values of -11.35 ± 0.04 (from five measurements) and -11.35 ± 0.02 (from four measurements) kcal mol⁻¹ were obtained from the one-buret method and the two-buret method, respectively, and agree with the accepted literature value (-11.33 kcal mol⁻¹).²⁴

Table II. $\Delta H_{1,1}$ (kcal mol⁻¹) for *p*-Anisidine-Cl₃CCO₂H System^a at 25 °C

	Single-buret method			Double-buret method
	Initial slope method		End point method	
	Our value	Mead's value	Our value	
Acid into base	-17.4	-18.8 (at 28 °C)	-16.4	-16.1
Base into acid	-20.8		-16.1	

^a Final concentration 2×10^{-2} M.**Table III.** Enthalpies of Pyridine-TFA System in CCl₄ at 25 °C

ΔH , kcal mol ⁻¹	One-buret method	Two-buret method
$\Delta H_{1,1}$	-8.9 ± 0.1	-9.0 ± 0.1
$\Delta H_{2,1}$	-9.0 ± 0.2	-9.3 ± 0.1
$\Delta H_{1,2}$	-14.7 ± 0.2	-14.9 ± 0.2

A comparison of the two-buret method with the one-buret method was provided by repeating the titration of the *p*-anisidine-Cl₃CCO₂H system in benzene at 25 °C as reported originally by Mead.³⁰ The ΔH values obtained are shown in Table II.

These results show that the initial slope method of Hume gives differing values depending upon the process (acid into base or base into acid). This was further supported by the fact that $\Delta H_{1,2}$ (-18.7 kcal mol⁻¹) obtained for this system by the two-buret method was different from that of $\Delta H_{1,1}$ (-16.1 kcal mol⁻¹) whereas Mead found $\Delta H_{1,2}$ and $\Delta H_{1,1}$ to be identical for this system. In all other cases studied by us and reported in Table I we find $\Delta H_{1,2}$ to be greater than $\Delta H_{1,1}$ for reasons to be presented in the Discussion. We expect that the same would hold for *p*-anisidine.

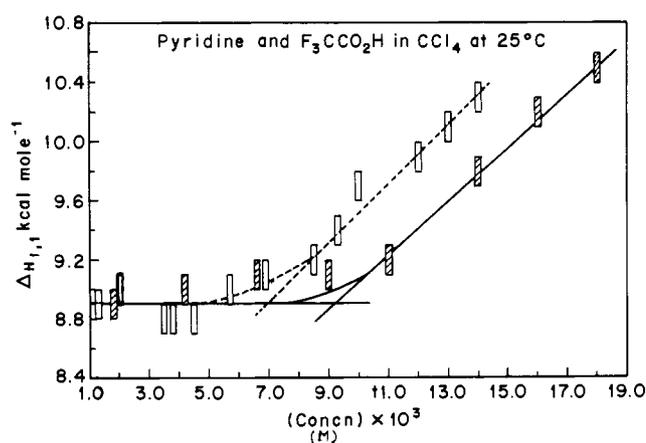
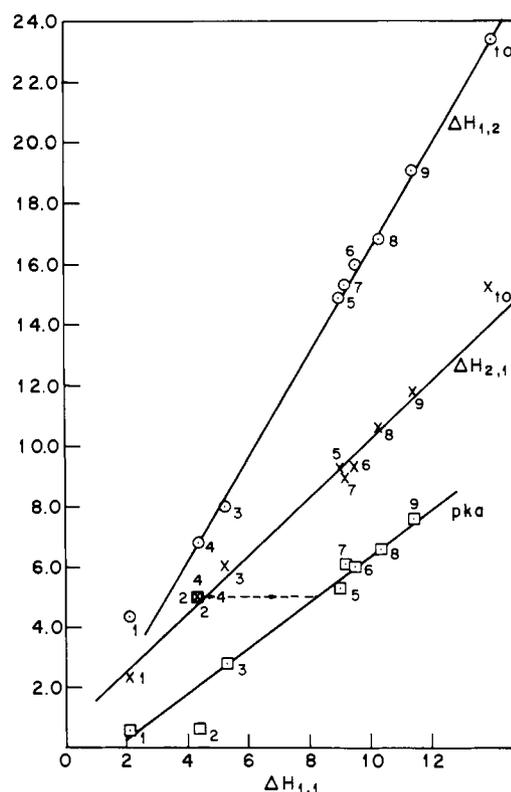
The pyridine-TFA system in CCl₄ at 25 °C was studied thoroughly by both methods. The comparison is shown in Table III as well as in Figure 2.

The dependence of $\Delta H_{1,1}$ upon concentration was examined. No significant variation was found within the concentration range of 1×10^{-3} to 6×10^{-3} M whereas considerable variation is found at higher concentrations. Thus, the -9.0 kcal mol⁻¹ value shown for $\Delta H_{1,1}$ in Table III goes to -10.5 kcal mol⁻¹ with a change of concentration from 1.5×10^{-3} to 1.8×10^{-2} M as shown on Figure 2. We are unable to account for the small systematic difference between the one- and two-buret methods at higher concentrations, but expect that it is an instrument error of some kind. Since most of our measurements were made at low concentrations it should not affect our results.

Discussion

The two-buret titration method employs simultaneous addition of stock solutions of acid and base to initially pure solvent. It deliberately avoids the normal enthalpimetric procedure of searching for stoichiometric break points on the thermogram in favor of maintaining a constant stoichiometric ratio of acid and base whose concentrations increase at a constant proportion. We have shown in the Results section that when all other terms, especially concentration, are equivalent the enthalpy of reaction obtained from the constant slope of the *linear* two-buret thermogram is consistent with the corresponding stoichiometric *end point* obtained from the normal single buret thermogram as it passes through the relative acid:base concentration represented by that stoichiometry.

It should be clear, however, from what is known of the many

**Figure 2.** Variation of $\Delta H_{1,1}$ for pyridine-TFA reaction as a function of concentration for one-buret and two-buret methods. ■, one-buret method, □, two-buret method.**Figure 3.** Correlation of $\Delta H_{1,1}$ with $\Delta H_{1,2}$, $\Delta H_{2,1}$, and pK_a for amines in Table I. Enthalpies are in kcal/mol; pK_a s are in pK_a units.

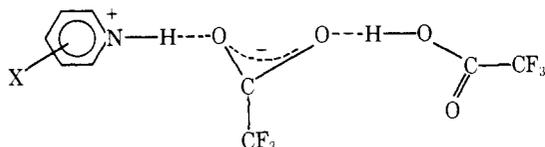
possible species in equilibrium in these solutions that the maintenance of a given stoichiometry in no way guarantees the quantitative formation of a complex species corresponding to that composition. Nonetheless, the results presented in Table I may be examined in the light of the limiting behavior of the species expected to be present.

First, we note a proportionality between the enthalpy terms $\Delta H_{1,1}$, $\Delta H_{1,2}$, and $\Delta H_{2,1}$ in Table I which is confirmed in Figure 3 where the latter two terms and the pK_a s of the corresponding pyridinium ion in water at 25 °C are plotted against $\Delta H_{1,1}$. The linear relationship including pK_a is no surprise since every other property known to us which is related to substituent effects on charging the pyridinium ring correlates with pK_a s. Only the point for the pK_a of 2,6-di-*tert*-butylpyridine (DTBP) falls off this line in conformity with its well-known low basicity in aqueous solution.³³ It is informative that

the enthalpies of the three different processes for titration in CCl_4 correlate so well with each other for all compounds, including DTBP. This implies that even if some of the reactions to form stoichiometric complexes are incomplete the corresponding free energies of formation are probably proportional to ΔH for that process, i.e., the driving force for completion is enthalpy controlled. This too is not surprising since one would expect very little effect from ring substitution on the relative entropy for each process. It is significant that even 2,6-di-*tert*-butylpyridine and 1,8-bis(dimethylamino)naphthalene, whose structures might be expected to favor or preclude some types of ion pairs more than the other bases listed here, fall within experimental error of the correlation lines.

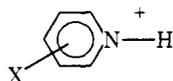
The original thermometric titration studies of Forman and Hume^{26,27} show that sharp end points, indicating complete neutralization of acid by base, are only found when the acid and base are strong—the most exothermic reactions are most complete. Accordingly, clearly defined processes will be most readily identified for the most exothermic amines in Table I. Furthermore, because of the proportionality noted above, the same conclusions which are inferred from the strongest bases may be applied to the weaker members of the series.

The most instructive means for comparing the stabilities of the three types of ion pairs comes from subtracting $\Delta H_{1,1}$ from $\Delta H_{1,2}$ and $\Delta H_{1,1}$ from $\Delta H_{2,1}$. The former difference represents the enthalpy for converting a simple 1:1 ($\text{BH}^+ - \text{A}^-$) ion pair into its acid-bound homoconjugate, 1:2 ($\text{BH}^+ - \text{AHA}^-$). The latter represents conversion of ($\text{BH}^+ - \text{A}^-$) to the base-bound homoconjugate ($\text{BH}^+ - \text{BA}^-$). Obviously, the formation of the ($\text{BH}^+ - \text{AHA}^-$) complex is by far the more exothermic process. Furthermore, as Figure 3 shows, the enthalpy of forming the acid-bound homoconjugate is directly proportional to $\Delta H_{1,1}$ as well as being nearly twice as great. Our interpretation is equivalent to that of Gol'dshtein et al.³¹ (who, however, put it in different terms) that these results are probably due to charge transfer of the electronic effects in the pyridinium ion through the intermediate TFA anion, thus:

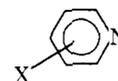


An electron-releasing group X will make the pyridine more basic relative to pyridine and will also make the ion-paired TFA anion more basic since the hydrogen bond from the cation will be weaker than in that from unsubstituted pyridinium ion. The obverse consequence results if X is electron attracting.

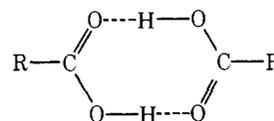
Considering now the values for $\Delta H_{2,1}$ representing formation of homoconjugate $\text{BH}^+ - \text{BA}^-$; they are chiefly significant in their similarity to $\Delta H_{1,1}$ which they exceed systematically by a small, and nearly constant, amount. Formation of the homoconjugate ion ($\text{BH}^+ - \text{B}$) in the case of tertiary amines such as the pyridines should remove the hydrogen bond from any further chance to interact with another base (or anion). Unlike the TFA anion, which has two basic oxygens, the pyridinium cation has but one acidic site. There is no opportunity for charge transfer such as we proposed for the ($\text{BH}^+ - \text{AHA}^-$) homoconjugate system. The fact that $\Delta H_{2,1}$ is slightly greater than $\Delta H_{1,1}$ simply means that the enthalpy released in forming the $\text{BH}^+ - \text{BA}^-$ homoconjugate ion pair is slightly greater than that required to separate the $\text{BH}^+ - \text{A}^-$ ion pair. The near constancy of $\Delta H_{2,1}$ is attributable, we believe, to the strictly reciprocal relationship between the effect of substituent X on the ability of



to donate a hydrogen bond and of



to serve as an acceptor. A clear analogy is that of the carboxylic acid dimers,

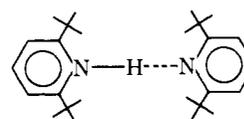


which maintain a nearly constant enthalpy of dimerization even though the strengths of the corresponding acids, RCOOH , vary considerably.¹⁷

Sterically Hindered Ion Pairs. 2,6-Di-*tert*-butylpyridine is renowned for its resistance to complexation by Lewis bases³³ and its reduced basicity in water.³⁴ Were it not for steric effects on protolysis we could expect from gas-phase results³⁵ that $\Delta H_{1,1}$, etc., for 2,6-DTBP would be large, probably comparable to that for 2,4,6-trimethylpyridine.³⁶ However, it is actually very low. If no proton transfer were occurring, we might expect some hydrogen-bonding interaction from TFA, perhaps to the π system of the ring which could account for the small exothermic value of $\Delta H_{1,1}$. However, if this were the case it is hard to see why its relationship to $\Delta H_{1,2}$ and $\Delta H_{2,1}$ would follow the pattern of the other pyridines as shown in Figure 3.

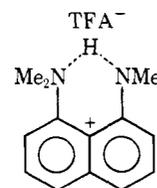
The infrared spectrum of the 1:1 mixture of 2,6-DTBP and TFA shows the customary sharp maximum at 3275 cm^{-1} , for the non-hydrogen-bonded pyridinium ion.³² We suggest that in a 1:1 mixture of 2,6-DTBP and TFA only a fraction, perhaps a third, of the acid and base react by proton transfer and that only a fraction of the ionized material is hydrogen bonded to the anion. When a second equivalent of acid or base is added the reaction is driven somewhat more to completion. This accounts for the proportionality between $\Delta H_{1,1}$ and $\Delta H_{1,2}$ and $\Delta H_{2,1}$ which is maintained, even in this case. We note in the latter case that formation of the ($\text{BH}^+ - \text{B}$) type of homoconjugate must be completely out of the question here.

As a rough analogue for this unstable homoconjugate



we have run a thermometric titration of 2,6-DTBP with 2,6-di-*tert*-butylphenol (as a crude model for the 2,6-DTBP cation) and detect no heat of reaction within experimental error.

Finally, we note the highly exothermic enthalpy values for Proton Sponge. We expect that the proton in this ammonium ion is so heavily shielded from the TFA anion and so nicely stabilized by its bidentate environment that its TFA^- counterion is virtually free of hydrogen bonds. The latter is therefore



very basic which explains the large exothermic effect when a second equivalent of TFA is added to produce the 1:2 homoconjugate.

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knowledge the original suggestion of the two-buret method by Craig Petro and Edward Mitchell.

Reference and Notes

- M. M. Davis, "Acid-Base Behavior in Aprotic Solvents", NBS Monograph 105, U.S. Government Printing Office, 1968. See also M. M. Davis, "The Chemistry of Nonaqueous Solvents", Vol. 3, Academic Press, New York, N.Y., 1970, Chapter 1.
- I. M. Kolthoff, *Anal. Chem.*, **46**, 1992 (1974); I. M. Kolthoff, *Bull. Soc. Chem. Belg.*, **84**, 501 (1975).
- J. E. Gordon, "The Organic Chemistry of Electrolyte Solutions", Wiley, New York, N.Y., 1975.
- J. S. Fritz, "Acid-Base Titrations in Nonaqueous Solvents", Allyn and Bacon, Boston, Mass., 1973.
- I. Gyenes, "Titration in Non-aqueous Media", D. Cohen and I. T. Milar, Ed., Van Nostrand, Princeton, N.J., 1968.
- W. Hubar, "Titrations in Non-aqueous Solvents", translated by Express Translations Service, London, Academic Press, New York, N.Y., 1967.
- J. Kucharsky and L. Sajarik, "Titrations in Non-aqueous Solvents", translated by K. Sumner, Elsevier, Amsterdam, 1965.
- G. M. Barrow, *J. Am. Chem. Soc.*, **78**, 5802 (1956).
- G. M. Barrow and E. A. Yerger, *J. Am. Chem. Soc.*, **76**, 5247 (1954).
- G. M. Barrow and E. A. Yerger, *J. Am. Chem. Soc.*, **76**, 5211 (1954).
- E. A. Yerger and G. M. Barrow, *J. Am. Chem. Soc.*, **77**, 6206 (1955).
- E. A. Yerger and G. M. Barrow, *J. Am. Chem. Soc.*, **77**, 4474 (1955).
- G. M. Barrow and E. A. Yerger, *J. Am. Chem. Soc.*, **76**, 5248 (1954).
- G. M. Barrow, *J. Am. Chem. Soc.*, **80**, 86 (1958).
- D. F. DeTar and T. W. Novak, *J. Am. Chem. Soc.*, **92**, 1361 (1970).
- Z. Dega-Szafran, E. Grech, M. Z. Naskret-Barciszewska, and M. Szafran, *J. Chem. Soc., Perkin Trans. 2*, 250 (1975).
- E. F. Caldin, *Q. Rev., Chem. Soc.*, **7**, 255 (1953).
- B. Chenon and C. Sandorfy, *Can. J. Chem.*, **36**, 1818 (1958).
- S. L. Johnson and K. A. Rumon, *J. Phys. Chem.*, **69**, 74 (1965).
- J. Barthel, "Thermometric Titration", Wiley, New York, N.Y., 1975.
- G. A. Vaughn, "Thermometric and Enthalpimetric Titrimetry", Van Nostrand-Reinhold, Princeton, N.J., 1973.
- H. J. V. Tyrrell and A. E. Beezer, "Thermometric Titrimetry", Chapman and Hall, London, 1968.
- S. Bark and S. M. Bark, "Thermometric Titrimetry", Pergamon Press, Elmsford, N.Y., 1969.
- D. J. Eatough, J. J. Christensen, and R. M. Izatt, "Experiments in Thermometric Titrimetry and Titration Calorimetry", Brigham Young University Press, Utah, 1974.
- D. J. Eatough, J. J. Christensen, and R. M. Izatt, *Thermochim. Acta*, **3**, 203, 219, 233 (1972).
- E. J. Forman and D. N. Hume, *J. Phys. Chem.*, **63**, 1949 (1959).
- E. J. Forman and D. N. Hume, *Talanta*, **11**, 129 (1964).
- J. Keily and D. N. Hume, *Anal. Chem.*, **36**, 543 (1964).
- J. Keily and D. N. Hume, *Anal. Chem.*, **28**, 1294 (1956).
- T. E. Mead, *J. Phys. Chem.*, **66**, 2149 (1962).
- I. P. Gol'dshtein, E. N. Gur'yanova, and T. I. Perepelkova, *Zh. Obshch. Khim.*, **42**, 2091 (1972).
- (a) E. M. Arnett, B. Chawla, and N. J. Hornung, *J. Am. Chem. Soc.*, submitted; (b) E. M. Arnett and B. Chawla, *ibid.*, submitted.
- H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **88**, 986 (1966).
- See H. P. Hopkins and S. Z. Ali, *J. Am. Chem. Soc.*, **99**, 2069 (1977), for citations to previous literature referring to the basicity of this compound.
- J. F. Wolf, P. G. Harch, and R. W. Taft, *J. Am. Chem. Soc.*, **97**, 2904 (1975).
- We estimate a $\Delta H_{1,1} = -11.4$ kcal/mol as the value to be expected for this compound in the absence of steric effects from a linear plot of $\Delta H_{1,1}$ for the other compounds vs. their gas-phase basicities, ΔG_i (gas).⁵⁵

Hydrogen Bond Strengths from Solvent-Dependent Lifetimes of Rose Bengal Dye

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Abstract: We report fluorescence lifetimes for rose bengal in a number of protic and aprotic solvents. The technique for obtaining these lifetimes uses time correlated photon counting with tunable dye laser excitation. The lifetimes ranged from 77 ps in $\text{CF}_3\text{CH}_2\text{OH}$ to ~ 2.5 ns in the aprotic solvents. We propose a linear correlation of the logarithm of the singlet-triplet decay lifetime, $\ln \tau_{\text{NR}}$, with the ΔH of hydrogen bonding of solvent to the oxygen anion site of rose bengal. Such a correlation might result from the linear relationship between the logarithm of the nonradiative lifetime, $\ln \tau_{\text{NR}}$, and the difference between singlet and triplet solvation energies. In this model the observed trend is that stronger hydrogen bonding molecules have larger rates of singlet to triplet intersystem crossing. The correlation is tested with the data available on relative hydrogen bond strengths to several bases. By using $\ln \tau_{\text{NR}}$ of rose bengal, one can order the relative hydrogen bond strengths for proton donors with very high precision. Absolute enthalpies for different proton donors can be found by obtaining the ΔH of hydrogen bonding for any two donors with the base of interest. In general, the hydrogen bond order of a series of proton donors is independent of base. In addition, the strongest hydrogen bond in a series of RXH molecules is formed by a molecule having the strongest XH bond. The picosecond lifetimes of rose bengal in various solvents are given in parentheses: $\text{CF}_3\text{CH}_2\text{OH}$ (77), H_2O (118), $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (473), $\text{HOC}_2\text{H}_4\text{OH}$ (481), CH_3OH (543), $\text{HOC}_3\text{H}_6\text{OH}$ (566), HC(O)NH_2 (686), $1\text{-C}_3\text{H}_7\text{OH}$ (739), $\text{C}_2\text{H}_5\text{OH}$ (739), $1\text{-C}_4\text{H}_9\text{OH}$ (773), $2\text{-C}_3\text{H}_7\text{OH}$ (975), HC(O)NHCH_3 (1020), $2\text{-C}_4\text{H}_9\text{OH}$ (1040), $(\text{CH}_3)_3\text{COH}$ (1240), CH_3CN (2380), CH_3COCH_3 (2570), $\text{HC(O)N(CH}_3)_2$ (2190).

Introduction

The fluorescence lifetimes of organic dye molecules can be sensitive to solvent environment for a variety of reasons. Several laboratories have recently found that halogen-substituted xanthene dyes have solvent-dependent lifetimes.^{1,2} For one of these dyes, erythrosin B, the singlet state is coupled to a lower triplet state and the sum of fluorescence and triplet yield has been shown to be near unity.^{3,4} Rose bengal is a tetraiodo-substituted xanthene dye, similar to erythrosin B, with the structure shown in Figure 1. The peak of the absorption spectra is near 558 nm and is slightly solvent dependent. Fluorescence lifetimes and reorientation times for rose bengal have been measured by one group of workers² in H_2O , CH_3OH ,

$\text{C}_2\text{H}_5\text{OH}$, and $2\text{-C}_3\text{H}_7\text{OH}$. We have found different values for the lifetime in these solvents and will discuss possible reasons later in this paper.

Although many of the details of our laser system have been described previously,^{5,6,7} we have not provided a complete description of the techniques necessary for performing short lifetime measurements in solution. Therefore, we have included a complete outline of our experimental technique.

Experimental Section

Tunable Dye Laser. An 8-W Ar^+ laser is used to pump a three mirror dye laser cavity. The jet stream solvent is ethylene glycol. For this series of experiments the laser dye Rhodamine 560 (from Exciton