of the labeled compound are indistinguishable from those at 134 and 119 for the unlabeled compounds; thus no rearrangement occurred during the synthesis and the C^{13} is in the α-position exclusively.

3-Ethyl-3-phenylpentane and 3-Ethyl-3-phenylpentane-1-*d*.—3-Ethyl-3-phenylpentane and 3-ethyl-3-phenylpentane-1-*d* were prepared from phenylpropane and 3-phenylpropane-1-*d* by sodium-catalyzed ethylation.[19] The unlabeled product boiled at 132° (50 mm.), $n^{20}D$ 1.5015; the labeled at 130° (50 mm.), $n^{20}D$ 1.5015. The mass-176 peak in the spectrum of the labeled product was attributed to the unlabeled compound, and the spectrum was corrected accordingly. The 3-phenylpropane-1-*d* was 96 ± 1% labeled; the 3-ethyl-3-phenylpentane-1-*d* was 91 ± 1% labeled. 3-Phenylpentane-1-*d* isolated from the synthesis was 92 ± 1% labeled.

Acknowledgment.—The authors thank D. L. Esmay, Peter Fotis and C. J. Norton for help in the syntheses.

WHITING, INDIANA

---

[19] H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, 77, 554 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

The Nature of Hydrogen Bonded Ion-Pairs: The Reaction of Pyridine and Carboxylic Acids in Chloroform

BY GORDON M. BARROW

RECEIVED MAY 23, 1956

The determination of relative base strengths from the equilibrium constants from the reaction of acids and bases in a non-dissociating solvent is shown to require a detailed understanding of the nature of the reaction product. A series of carboxylic acids are studied for which the weakest and strongest acids form, respectively, a simple hydrogen bonded complex and an ion-pair salt with the base pyridine. The infrared spectra of the 1:1 reaction products of acids of intermediate strength with pyridine show these products to consist of a simple hydrogen bonded complex in tautomeric equilibrium with an ion-pair species rather than a single resonating species. For the acids studied a 2:1 reaction product is shown to exist only for an ion-pair species. The equilibrium constants for the reaction of pyridine and acetic acid in CCl_4 and $CHCl_3$ are reported and are compared with the results for other bases.

The reaction of protonic acids with bases in non-dissociating solvents leads, for acids and bases of sufficient strength, to the formation of an ion-pair salt associated through a hydrogen bond.[1-3] For such systems the acidic proton is said to be transferred and the hydrogen bonding back to the anion is considered to be essentially electrostatic. For weaker acids and bases[4,5] in similar solvents the reaction product consists of a simple hydrogen bonded complex. In these cases the proton is considered to remain covalently bonded to the acid and the base is associated to the acidic hydrogen through an electrostatic attraction. It is of interest to consider here the distinction between these two extreme situations and to inquire into the nature of the reaction in non-dissociating solvents between protonic acids and bases of intermediate strength.

This intermediate case can be considered as a structural problem involving the equilibrium position, or positions, of the proton through which the acidic and basic groups are associated. For a proton equally attracted to the parent acid and to the base the potential energy can be represented either by a curve with a single minimum between the two groups or by a curve with two minima, each minimum approximately a covalent bond length from each of the two groups. Neither possibility can be immediately ruled out. It now appears that for a number of hydrogen bonds in crystalline materials the single minimum is more probable.[6] The only suitable comparison, where the groups are not held in a crystal lattice, would appear to be in the system of a hydronium ion associated to a water molecule.[7] Although the many complexities of this system allow only a remote comparison, it is of interest to note the probable existence of a double minimum with the proton attached to one or the other of the adjacent water molecules.

This question of the nature of the acid–base reaction product bears on the study of acid and base strengths in non-dissociating solvents. Equilibrium constant studies, to determine relative base strengths have been made by Bell and Bayles[1] in which the reaction results in a proton transfer. It is customary, also, to make use of shifts in the acidic OH frequency to estimate base strengths where the proton is not transferred.[4] Two potential difficulties are introduced by these approaches.

It is, firstly, necessary to know if equilibrium constants obtained at the two extremes are to be taken as limiting examples of the same type of reaction or whether they represent results for two essentially different reactions. The first would apply if, for increasing acidity and basicity, the potential minimum for the proton shifted continuously from a position near the acid to one near the base *i.e.*, if the single minimum potential was appropriate. If, on the other hand, a double minimum applies, the proton transfer and simple hydrogen bonding reactions are different reactions and no straightforward comparison of the results of the two reactions with each other, or with the base strength, can be expected. It follows, therefore, that comparison of acids or bases with a wide range of strengths in non-dissociating solvents by means of equilibrium constants requires a detailed understanding of the reaction product.

---

[1] R. P. Bell and J. W. Bayles, *J. Chem. Soc.*, 1518 (1952).

[2] M. M. Davis and H. B. Hetzer, *Bur. Standards J. Research*, **48**, 381 (1952).

[3] G. M. Barrow and E. A. Yerger, THIS JOURNAL, **76**, 5211 (1954); **77**, 4474 (1955); **77**, 6206 (1955).

[4] W. Gordy, *J. Chem. Phys.*, **9**, 215 (1941).

[5] M. Tamres, S. Searles, E. M. Leighly and D. W. Mohrman, THIS JOURNAL, **76**, 3983 (1954).

[6] R. E. Rundle and M. Parasol, *J. Chem. Phys.*, **20**, 1487 (1952).

[7] B. E. Conway, J. O'M. Bockris and H. Linton, *ibid.*, **24**, 834 (1956).

The second question bears on the choice of meaning to be assigned to "base strength." Customarily this is related to the amount of acid and base reacting at a given concentration. If, for various acids and bases, there is a gradual transition of the proton from the acid to the base it would also be feasible to consider the acid or base strength, in non-dissociating solvents, in terms of the extent of proton transfer in the reaction product. This alternate description of base strength would, however, have no value for an extended range of acid and base strengths if the proton experiences a double minimum potential.

The nature of the problem, *i.e.*, the location of the proton, precludes the use of most direct physical methods. It is possible, however, to study the properties of the reaction product of a base with acids of various strengths and from the variation in these properties to deduce the nature of the change in the reaction products. A suitable system is that of pyridine reacting with various substituted acetic acids in the solvent chloroform. The reaction products are conveniently characterized by their infrared spectra.

Experimental

The infrared spectra were obtained on a Baird Associates Instrument with rock salt optics. A cell thickness of 0.1 mm. was convenient for all solutions, which had a concentration of about 0.1 *M*. The wave lengths reported were read off spectra with a superimposed polystyrene calibration spectrum.

Spectra for two types of titrations were obtained. The spectra of solutions 0.1 *M* in acid and with various concentrations of pyridine revealed the nature of the variation in the acid group as it reacted with the base. To more easily interpret the variations in the pyridine as it was transformed to the product, spectra were obtained with a fixed pyridine concentration of 0.2 *M* and various acid concentrations.

The approximate temperature dependence of the absorption bands of a solution of 0.4 *M* dichloroacetic acid and 0.4 *M* pyridine in $CHCl_3$ was obtained by warming the cell to 55° in an oven and immediately recording the short range of spectrum required. These qualitative temperature results were sufficient for the present purpose.

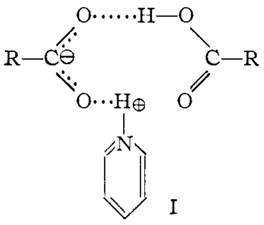
The solvent $CHCl_3$ used was washed with sulfuric acid, sodium carbonate solution and water. It was then dried over Drierite and distilled under nitrogen.

The acetic acid was prepared by addition of the calculated amount of acetic acid to J. T. Baker analyzed reagent grade acetic acid to give the anhydrous material. Dichloro- and trifluoroacetic acid, from Eastman Kodak, were distilled in a dry nitrogen atmosphere and a constant boiling center cut used. Trichloroacetic acid, from Eastman Kodak, was vacuum sublimed. Iodoacetic acid, Eastman Kodak, was fractionally crystallized from $CHCl_3$–CCl_4 mixtures to give a slightly yellow crystalline material. Chloropropionic acid, Eastman Kodak, and chloroacetic acid, Matheson, were used without purification.

Pyridine was distilled in a 30 cm. packed column and stored over KOH.

Results and Discussion

The Nature of the Intermediate Species.—In the titration of $CHCl_3$ solutions of 0.1 *M* trifluoroacetic acid and trichloroacetic acid a species [pyridine·$(HA)_2$] is formed stoichiometrically for pyridine concentrations up to 0.05 *M*. This species shows absorptions corresponding to the presence of both a carbonyl group and a carboxylate group. As suggested previously for the reaction of triethylamine and acetic acid,[3] the structure of this species can be written as



I

For weaker acids than these, the reaction to product I proceeds less completely and a 1:1 reaction product tends to be formed. For sufficient excess acid, however, it is possible to force the equilibrium to I except for acetic and β-chloropropionic acids. Iodoacetic and chloroacetic acids require an acid concentration of about 1 *M* with a pyridine concentration of 0.2 *M* to shift the equilibrium almost entirely to I and permit certain identification of the absorption bands of I. Table I shows some of these absorptions, attributable to I. The large excess of the weaker acids used prevents intensities being determined for some absorptions.

TABLE I

ABSORPTION MAXIMA IN MICRONS AND EXTINCTION COEFFICIENTS, $1/cl \log_{10}(I_0/I)$ IN L. MOLES^{-1} CM.$^{-1}$ IN BRACKETS FOR THE SPECIES $(HA)_2$·PYRIDINE

Acid	(C=O)	(CO_2^-)	($C_5H_5NH^+$)	
CF_3COOH	5.61	6.00	6.10	6.72
	(300)	(200b)	(40)	(200)
CCl_3COOH	5.74	6.09	6.11	6.72
	(300)	(200b)	(45)	(200)
CCl_2HCOOH	5.78	6.27	6.11	6.73
	(−)	(200b)	(−)	(200)
$CClH_2COOH$	5.80	6.35	6.11	6.73
	(−)	(160)	(45)	(180)
CIH_2COOH	5.85	6.41	6.12	6.73
	(−)	(160)	(−)	(160)

All these monomer–dimer species can be considered to have the proton-transferred ion-pair structures shown as I. The characteristic carboxylate band is the best direct evidence for this conclusion. The shift from the dimer acid carbonyl absorption wave length to that of the carboxylate band of I is shown as a function of the pK_a of the acids[8] in Fig. 1.

The pyridinium ion bands, furthermore, have almost the same frequency and intensity for all the acids, indicating an essential similarity in these products. On this basis the absorption bands listed in Table I for the pyridinium ion can be taken as characteristic of this ion. Further characterization is provided by the complete absence of the strong 6.97 μ band of pyridine in these reaction products. This band is, however, less useful because of the strong interference from small amounts of unreacted pyridine.

The Monomer Reaction Product.—Titration of a chloroform solution of pyridine by any of the

---

[8] The pK_a for CH_3COOH and $CClH_2COOH$ have been reported by J. F. J. Dippy, *Chem. Revs.*, **25**, 151 (1939); for ClH_2COOH and CCl_2HCOOH by F. Swarts, *Bull. soc. chim. France*, **35**, 1533 (1924); for CF_3COOH by A. L. Henne and C. J. Fox, THIS JOURNAL, **73**, 2323 (1951). The pK_a for CCl_3COOH has been estimated by H. C. Brown from the conductivity data of the "International Critical Tables," McGraw–Hill Book Co., New York, N. Y., 1929, Vol. VI, p. 259, from which also the result for $CClH_2CH_2COOH$ is obtained.

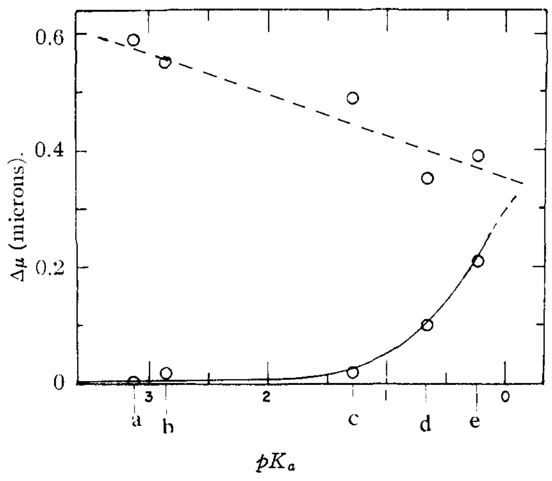


Fig. 1.—Wave length shift of the carbonyl absorption band from the dimer acid to the species [pyridine·(HA_2)] (dashed line) and to the species [pyridine·(HA)] (solid line) for: a, iodoacetic; b, chloroacetic; c, dichloroacetic; d, trichloroacetic; e, trifluoroacetic acids.

acids studied leads initially to the formation of a species of the form (pyridine·HA) represented as II. For the stronger acids CF_3COOH and CCl_3COOH this product is formed stoichiometrically at a one to one acid–base ratio. For the weaker acids an equilibrium constant calculation indicates the production of such a species as will be illustrated for acetic acid below.

The nature of this complex may be deduced from the spectra in the region of the carbonyl, carboxylate and pyridine ring vibrations for this reaction product as given, schematically, in Fig. 2. For the (pyridine·CF_3COOH) and (pyridine·CCl_3COOH) products the pyridinium ion absorption bands at about 6.12 and 6.72 μ are seen to be present and to have approximately the same peak intensity as found for I. This leads directly to the conclusion that a proton transfer process has occurred and we are here dealing with an ion-pair species. The weakest acids studied, however, show no absorption at these wave lengths indicating an essentially different reaction product. The gradual transition of a pyridine absorption band from 6.33 μ in CCl_4 to 6.24 for the pyridine–acetic acid complex as the hydrogen bonding is increased indicates that the weaker acids can be considered to form non-proton-transferred hydrogen bonded species, differing only in the degree of electrostatic attraction from the complexes with $CHCl_3$ and butyl alcohol. The acids CF_3COOH and CH_3COOH, therefore, produce the extreme types of acid–base products in $CHCl_3$ and those of intermediate strength will provide product species of particular interest.

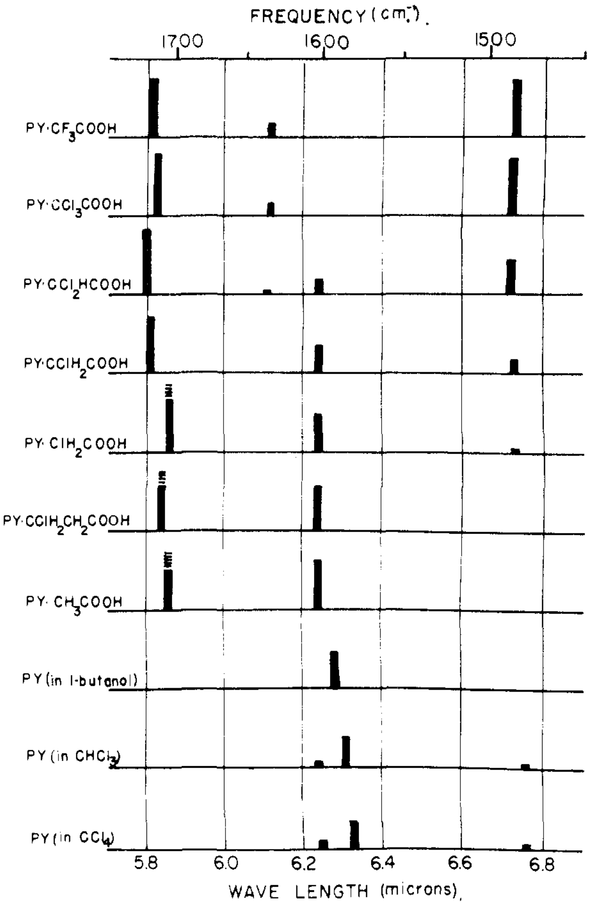


Fig. 2.—Absorption bands for the species [pyridine·(HA)] in $CHCl_3$ and for pyridine in the solvents CCl_4, $CHCl_3$ and 1-butanol. (The separation between horizontal lines corresponds to an extinction coefficient of 200.)

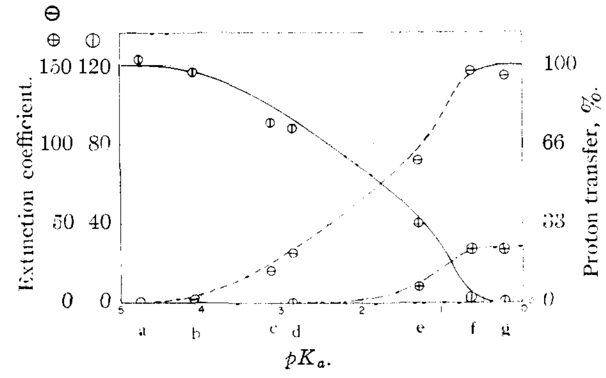


Fig. 3.—Optical densities, $\log_{10}(I_0/I)$, for the 6.24 μ band (⦶ and solid line) of the hydrogen bonded complex and the 6.72 μ (⊖ and dashed line) and 6.11 μ (⊕ and dash-dot line) bands of the ion-pair for the species [pyridine·(HA)] as a function of pK_a (a, acetic; b, chloropropionic; c, iodoacetic; d, chloroacetic; e, dichloroacetic; f, trichloroacetic; g, trifluoroacetic acids).

For the intermediate acid strengths it is convenient to have a more quantitative measure of the relative importance of the proton transfer and simple hydrogen bonded descriptions. The extinction coefficients, $1/cl \log_{10} I_0/I$, of the 6.72 and the weaker 6.11 μ bands can be used to measure the importance of the proton transfer while the 6.24 μ band can be used for the hydrogen bonded description. Figure 3 shows these extinction coefficients for the acids arranged according to their pK_a. Considerable scatter is to be expected due to the uncertainty in the extinction coefficients which arises principally from the general background absorption characteristic of these ion-pair like species.

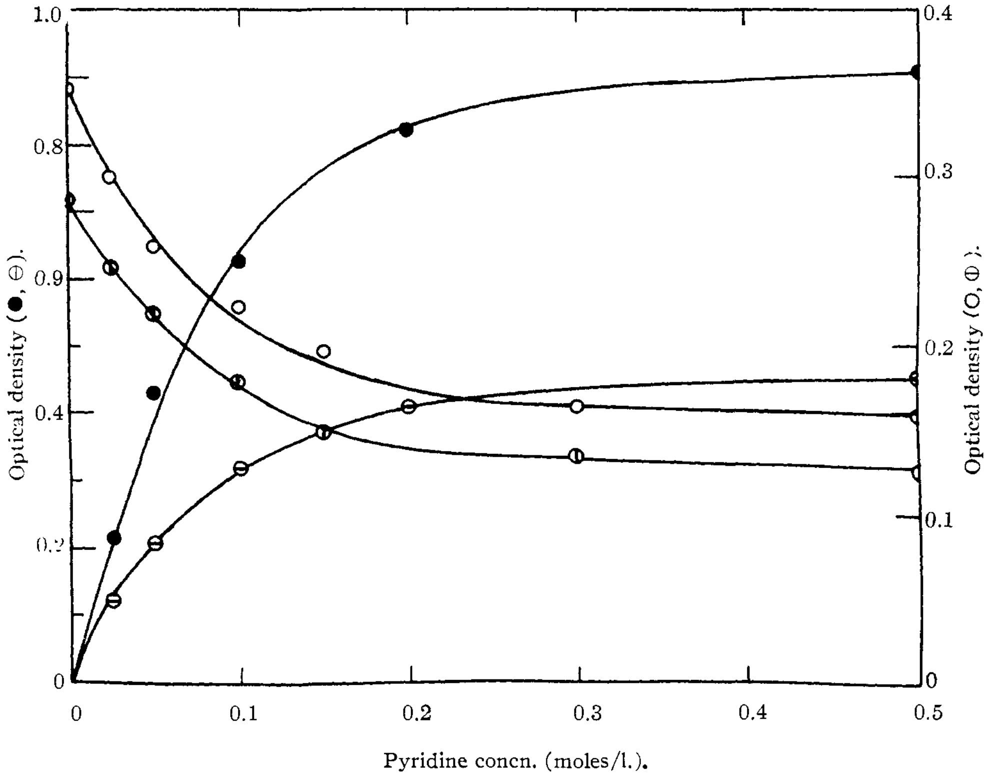
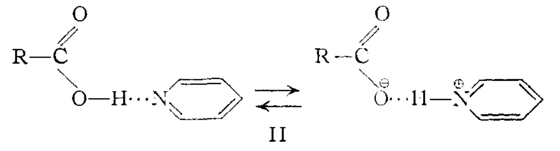


Fig. 4.—The optical densities in the pyridine–acetic acid system: ●, 7.88μ band in CCl_4, O, 5.85μ band in CCl_4; ⊖, 9.94μ band in $CHCl_3$, ⦶, 5.88μ band in $CHCl_3$.

The ordinates of Fig. 3 have been chosen and the curves drawn so that a per cent. ionic character or per cent. proton transfer scale can be added. It is necessary now to decide whether for dichloroacetic acid, for example, Fig. 3 should be interpreted as giving the percentage importance, to the electronic description of the single product species as 71% proton transfer and 29% hydrogen bonding or whether it indicates that 71% of the product species are of the proton transfer type and 29% are simple hydrogen bonded complexes. Two approaches to this question are possible through infrared spectroscopy.

The first concerns the effect of temperature. Again, for example, if the product with CCl_2HCOOH is a single species the per cent. proton transfer description, obtained from the relative extinction coefficient of the 6.72 and 6.24 μ bands, will likely be little affected by a change in temperature. For an equilibrium between a proton transfer species and a hydrogen bonded complex, however, it is possible for the temperature dependence to be appreciable. It is observed that for a temperature increase from 25 to 55° the intensity of the 6.24 μ band increased by about 45% while that of the 6.73 band decreased by about 16%. The weaker band at 6.12 μ appeared to increase in intensity. These changes correspond, from Fig. 3, to an increase of about 11% in the O–H character and a corresponding decrease in the H–N^+ character. This result is most easily compatible with the double minimum potential for the proton and a tautomeric equilibrium of the type



The second indication of tautomeric equilibrium is the lack of a gradually shifting absorption band frequency as the acid strength is varied. It appears unlikely that, if pyridine were to continuously take on the character of a pyridinium ion, the ring vibrations would not lead to one or more absorption bands whose frequency would vary continuously. The shifting of the 6.33 pyridine band in CCl_4 to 6.24 μ for the acetic acid complex is an example of such a gradation in type of product. For further acid strength increase, however, no such frequency trend results (see Fig. 2) and again the data are most easily interpreted as a disappearance of the hydrogen-bonded complex and the appearance of the quite different ion-pair species.

Only for the carbonyl–carboxylate absorption, 5.80 to 5.85 μ, is the situation less easily described. The wave length shift from the acid dimer carbonyl to the carbonyl–carboxylate of product II is shown in Fig. 1. Even for the products with trifluoro and trichloroacetic acids, which are clearly proton transferred ion-pairs, this wave length shift is much less than would be expected for a product with a free, symmetric carboxylate group. It appears, therefore, that this absorption position cannot be taken as a measure of the carbonyl–carboxylate character and that the absorption position is affected not only by the covalency of the O–H bond but also by the electrostatic attraction of the H–N$^+$ for one of the anion oxygens.[3] The absence of a split in this carbonyl–carboxylate absorption due to the tautomeric equilibrium can therefore be attributed to this averaging effect and the inherent broadness of this absorption band.

Equilibrium Constants for the Reaction of Acetic Acid and Pyridine.—The association of pyridine and acetic acid, although only a hydrogen bonding reaction, leads to sufficient changes in the spectra of acetic acid and pyridine to allow the calculation of an equilibrium constant for the reaction. Figure 4 shows a plot of the optical density, $\log_{10} (I_0/I)$, for several absorption bands for the titration of 0.05 *M* acetic acid with pyridine in CCl_4 and $CHCl_3$. The plotted curves are calculated for the reaction

$$2C_6H_5N + (CH_3COOH)_2 \rightleftharpoons 2(CH_3COOH{\cdot}C_6H_5N)$$

with $K = 40$. The fit with the experimental points for this pyridine concentration, and similar agreement for pyridine concentrations of 0.5 and 0.005 *M* support the conclusion that a monomer–monomer product is formed.

Combined with the dimerization equilibrium constants for acetic acid,[9] this result gives for the reaction

$$C_5H_5N + CH_3COOH \rightleftharpoons CH_3COOH{\cdot}C_6H_5N \quad K_{CCl_4} = 220 \quad K_{CHCl_3} = 70$$

It can be pointed out, now that this reaction has been shown probably to be different in kind to that occurring, for example, with triethylamine and acetic acid, that these equilibrium constants cannot be compared with those for a true proton transfer process to yield directly relative base strengths. The work of Tamres, Searles, Leighly and Mohrman[5] has already pointed out some of the effects resulting from possible courses of the reaction. Further indication of the different nature of the reaction of pyridine with acetic acid and of triethylamine and acetic acid is the fact that for the former the equilibrium constant for CCl_4 is about 3 times that for $CHCl_3$ while for the latter reaction the CCl_4 constant is about one quarter of that for $CHCl_3$. This result is readily rationalized on the basis of the solvent interaction expected for the two types of products.

Such comparisons, however, raise the question of the nature of the product of the reaction of acetic acid and triethylamine in CCl_4. It does not necessarily follow from the indications of pyridine that double potential minimum product will again be formed. It may well be that the triethylamine product has only a partial ion-pair character and equilibrium constant comparisons are therefore hazardous. It seems difficult, moreover, to establish the nature of this product from the infrared spectra.

If the double potential minimum for the proton applies also to bases other than pyridine the use of degree of proton transfer as a measure of base strength, as determined for example, by the OH stretching absorption frequency shift, can be applicable only for weak acids and bases which do not transfer the proton in the solvent used and the equilibrium constant criterion of acidity and basicity can be applied only within sets of reactions leading exclusively to ion-pair formation or to hydrogen bonded complexes.

EVANSTON, ILLINOIS

---

[9] G. M. Barrow and E. A. Yerger, THIS JOURNAL, **76**, 5248 (1954).