Proton Tunnelling in Acid–Base Systems in Nonaqueous Solvents

By DELOS F. DETAR* and RONALD NOVAK

(*Department of Chemistry and Institute of Molecular Biophysics, The Florida State University, Tallahassee, Florida* 32306)

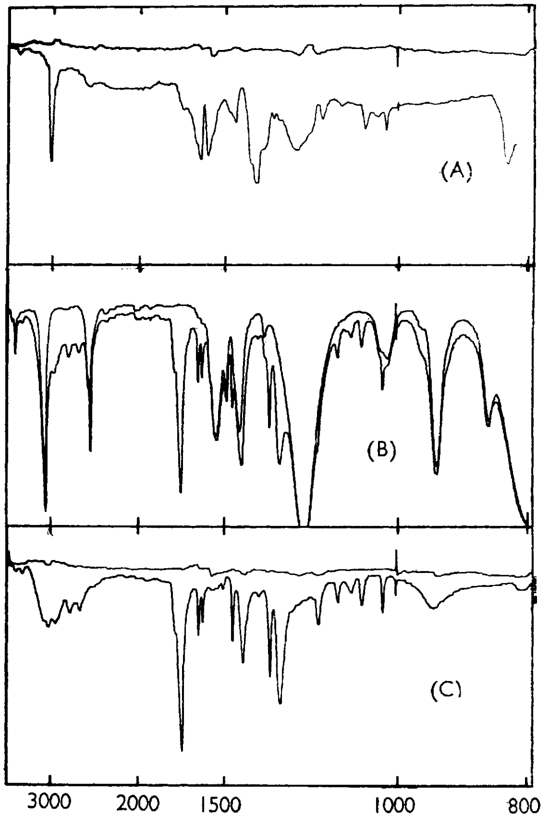
WE present spectral evidence pointing to the occurrence of extensive proton tunnelling in certain species present in the acid–base equilibria between carboxylic acids and triethylamine in solvents such as acetonitrile and chloroform. The literature on hydrogen bonding is voluminous. The pronounced broadening of i.r. bands has been ascribed to several causes, including proton tunnelling, but the field is controversial.[1] Our observations concern several new facts.

Acid–base equilibria in nonaqueous solvents may be summarized empirically in terms of a 1 : 1 complex (I) and a 1 : 2 complex (II).[2] Detailed studies have revealed two anomalies. Thus comparison of the curve for the acid–base mixture (Figure A) with

$$\begin{aligned} &Et_3N + RCO_2H \rightleftharpoons \\ &\qquad \underset{(I)}{Et_3N{\cdot}RCO_2H} + \underset{(II)}{Et_3N{\cdot}(RCO_2H)_2} \end{aligned}$$

the curves for benzoic acid (Figures B and C), for triethylamine (Figure D), for tetramethylammonium benzoate (Figure E), and for triethylammonium bromide (Figure F) shows that (I) and (II) lack such typical benzoic acid peaks as the carbonyl stretching band at 1714 cm.$^{-1}$ and have instead peaks characteristic of tetramethylammonium benzoate such as those at 1583 and 1619.† This result points to a triethylammonium benzoate (ion pair) structure for (I) and (II). However, the N–H peaks at 2509 and 2631 cm.$^{-1}$ characteristic of the triethylammonium group (Figure F) are virtually absent. Work with $PhCO_2D$ has also failed to show Et_3ND^+. This contradictory result argues against the postulated ion-pair structure.

The second anomaly is the pronounced shift of the I_0 portion of the curve. Comparison of the benzoic acid spectrum (Figures B and C) and the triethylamine spectrum (Figure D) shows that neither compound absorbs appreciably in the 2200—1800 cm.$^{-1}$ region. Yet a mixture of the two (Figure A) shows moderately strong general absorbance here, and indeed over most of the NaCl region, tapering off toward 3500 cm.$^{-1}$ This band is much broader than usually observed for hydrogen bonding. Careful investigation with a variety of window materials eliminated the possibility of trivial causes such as window contamination,



(A) *Benzoic acid* (0·065 M) *plus triethylamine* (0·059 M) *in chloroform, against chloroform. Cell thickness* 0·2 mm; *sodium chloride. Same cell for all curves except Figure* 5. *Perkin-Elmer Model* 21, *slave recorder. Ordinate is per cent transmittance.*

(B) *Chloroform and* 0·064 M-*benzoic acid in chloroform* (*not compensated so as to show solvent absorption*).

(C) *Upper curve solvent, against solvent. Lower curve* 0·064 M-*benzoic acid in chloroform against chloroform.*

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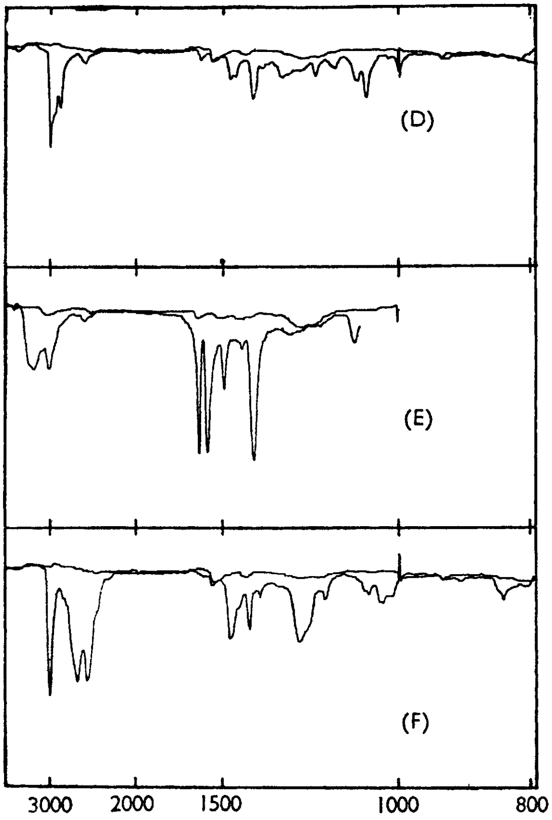
† Details of the spectra of acid–base mixtures, and accordingly the relative concentrations of various species, are sensitive to solvent, particularly to solvent hydrogen-bonding properties.

precipitation, or reaction with spacer. Qualitatively the general absorbance for a given acid concentration increases with increasing amounts of triethylamine up to a limiting value. Quantitatively it must be ascribed both to salt (I) and to salt (II) with a larger molar absorbancy index for salt (I). The extent of this broad absorption pattern depends on the acid–base system. A number of carboxylic acids behave similarly to benzoic acid, but with an approximately 1 : 1 mixture of the strong acid trifluoroacetic acid with triethylamine the general absorbance is restricted to the narrower region of about 3000—1500 cm.$^{-1}$. Furthermore, neither triethylammonium picrate nor mixtures of triethylamine with triethylammonium bromide show appreciable general absorbance.



(D) *Triethylamine* (0·057 M) *in chloroform, against chloroform.*

(E) *Tetramethylammonium benzoate* (0·037 M) *in chloroform* + 2% *ethanol, against chloroform* + 2% *ethanol. Cell thickness* 0·2 mm; *calcium fluoride. The ethanol was used to increase solubility. Except for the OH peak at* 3300 cm.$^{-1}$, *the spectrum is the same as that of more ragged curves using dilute solutions without ethanol.*

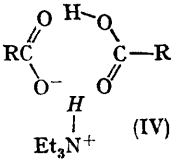
(F) *Tetraethylammonium bromide* (0·065 M) *in chloroform, against chloroform.*

Proton exchange broadening is commonplace in n.m.r. where the time scale is of the order of milliseconds. Comparable exchange in the i.r. region involves relaxation times of the order of 10^{-14} sec., and can occur only under special conditions. We suggest that these conditions are fulfilled in the carboxylic acid–base systems and that proton exchange *via* tunnelling accounts for both anomalies.

As a condition for tunnelling, the proton shown in italic in (III) and in (IV) must have available two or possibly several potential wells of nearly the same energy and separated by a low activation energy barrier. The disappearance of most of the I–H · · · O acid dimer absorbance upon addition of about 0·5 mole of triethylamine to 1·0 mole of benzoic acid indicates that the O–H–O proton in (IV) may also be tunnelling. The extent of the general absorbance presumably implicates bending as well as stretching vibrations.

$RCO_2^{-}\mathit{H}NEt_3$

(III)



(IV)

Our investigations are directed primarily to an understanding of the equilibrium stoicheiometry of acid–base systems and suggest that the phenomena will prove valuable auxiliary tools whatever their ultimate theoretical basis.

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[1] See *e.g.*, G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", W. H. Freeman and Co., San Francisco, California, 1960, pp. 104, 246; Early theoretical suggestions of proton tunnelling in hydrogen bond systems have been reviewed: C. G. Cannon, *Spectrochim. Acta*, 1958, **10**, 341 (see page 354); S G. W. Ginn and J. L. Wood, *J. Chem. Phys.*, 1967, **46**, 2735; L. J. Bellamy and P. E. Rogasch, *Proc. Roy. Soc.*, 1960, *A*, **505**, 98.

[2] See D. F. DeTar and R. Silverstein, *J. Amer. Chem. Soc.*, 1966, **88**, 1020, for a brief bibliography; G. M. Barrow, *ibid.*, 1956, **78**, 5802; G. M. Barrow and E. A. Yerger, *ibid.*, 1954, **76**, 5211; and other papers in this series; P. J. R. Bryant and A. W. H. Wardrop, *J. Chem. Soc.*, 1957, 895.