Tetrahedron Letters No.50, pp. 4553-4555, 1965. Pergamon Press Ltd.
Printed in Great Britain.

THE ACIDITY OF ACETIC ACID -d.

Neil S. Isaacs
University of Victoria, Victoria, B.C.

(Received 19 October 1965)

Water is well known to be less acidic than deuterium oxide(1,2) but no information is available as to the relative extent of acid-base dissociations in pure acetic acid and acetic acid-d. Calculation of the increase in zero-point energy when equations 1 and 2 proceed to the right, using values of the vibrational frequencies of the affected bonds set out in Table 1, leads to a value for the deutero acid slightly greater (by about 120 cm^{-1}) than that for protio acetic acid. This would indicate that the latter is the stronger acid by a small margin. The difference in these values, however, is too small to be able to place any reliance on this conclusion owing to the approximate nature of such calculations and the neglect of differences in hydrogen bonding effects and the partition functions for each equilibrium.

$$CH_3COOH + R_3N \rightleftharpoons CH_3COO^- + R_3NH^+ \qquad 1$$

$$CH_3COOD + R_3N \rightleftharpoons CH_3COO^- + R_3ND^+ \qquad 2$$

In order to ascertain the relative acidities of acetic acid and its deuterium analogue, we have measured by a spectrophotometric technique(3) the dissociations in these media of two indicators, N, N-dimethyl-p-nitroaniline(4) and N,N-dimethyl-p-bromoaniline(5) both of which are incompletely dissociated. In either case, the intensity of the n - π* transition due to the free base was measured and found (Table 2, Fig. 1) to be greater in the deutero acid as predicted.

TABLE 1.

Vibrational Frequencies (cm^{-1})

X	X-H str.	X-D str.	X-H def.(2)	X-D def.(2)
$CH_3CO.O-$	3500	2300	940	700
$Ph\overset{+}{N}Me_2-$	3400	2120	1620(6)	1540(6)

To obtain values of the equilibrium constants K_H and K_D it is necessary to have absolute extinction coefficients for both the free base and conjugate acid forms of each indicator. The latter is obtainable from the spectra of solutions in 0.1 M sulphuric acid in acetic acid. The free base was examined from solutions of indicator in acetic acid containing potassium acetate. Under these conditions, spectra of N,N-dimethyl-p-nitroaniline reached a constant extinction coefficient at the absorption maximum in the presence of 0.3 M acetate ion but this was not observed with the slightly stronger base N,N-dimethyl-p-bromoaniline. The conjugate base of this indicator was therefore studied in ethanol where, it was assumed, solvation conditions sufficiently similar to those in acetic acid exist. This assumption was strengthened by the observation that the shape and position of the absorption maxima were not noticeably different in the two solvents(6).

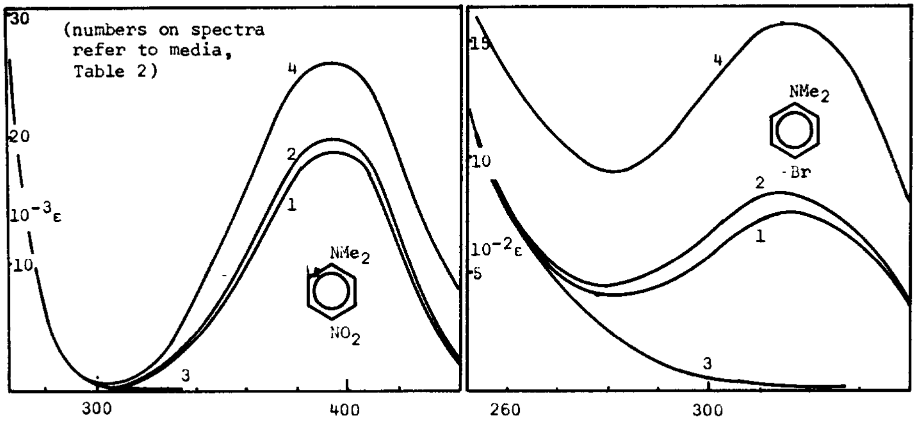
TABLE 2.

	p-Nitro-N,N-dimethylaniline (λ_{max}=397mμ.)		p-Bromo-N,N-dimethylaniline (λ_{max} = 315mμ.)	
medium	ε *	% free base	ε *	% free base
1 CH_3COOH	18,810	71.8	761	47.2
2 CH_3COOD	20,060	76.7	857	53.5
3 0.1 M H_2SO_4	0	0	37	0
4 0.35M KOAc in AcOH	26,110	100	1570**	100

* at °C

** in ethanol

Fig. 1



We conclude that protonation of a weak base in acetic acid occurs to an extent approximately 10% greater than in the deutero analogue. It would therefore be anticipated that a solvolytic reaction in acetic acid proceeding by the rate-determining decomposition of the conjugate acid of the substrate would be subject to a solvent isotope effect and would be somewhat slower in acetic acid-d. This prospect is presently under examination.

REFERENCES

(1) J. Bigeleisen and M.G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947)

(2) K. Wiberg, *Physical-Organic Chemistry*, Wiley, New York (1964)

(3) L.P. Hammett and A.J. Deyrup, *J. Am. Chem. Soc.*, **54**, 2721, 4239 (1932)

(4) B.M. Bogoslovsky, *Zhur. Obshchei Khim.* **24**, 922 (1954)

(5) G.M. Kosolopoff, *J. Am. Chem. Soc.*, **75**, 3596 (1953)

(6) H.H. Jaffe and M. Orchin, Theory & Application of Ultraviolet Spectroscopy, Wiley, New York, p. 186-189 (1962)

ACKNOWLEDGEMENT

The National Research Council of Canada are thanked for financial support of this work.