

**699.** *Infrared Studies of the Deuterium Isotope Effect in Acids.*

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Measurements have been made of the OH and OD stretching frequencies of aliphatic carboxylic acids in a number of solvents. These are shown to be related to  $pK_H$  and  $pK_D$  of the acids, enabling  $pK_H$  and  $pK_D$  to be predicted for acids of this type from spectroscopic data. These results further provide relative acidity values for [H]- and [D]-acids in non-aqueous solvents.

The observed spectroscopic isotope effects are explained in terms of anharmonicity of the particular OH vibration.

THE isotope effect resulting on substitution of deuterium for hydrogen in carboxylic and other acids results in a ratio  $K_H : K_D > 1$ . This ratio increases with decreasing acid strength, varying from 1.71<sup>1</sup> for phosphoric acid ( $K_1$ ) to about 6.5<sup>2</sup> for water. It has been suggested<sup>2,3</sup> that the effect originates in the difference and changes in zero-point energies for the two acids, and calculations by Bunton and Shiner<sup>4</sup> confirm this when allowance is made for changes in hydrogen bonding in the process of dissociation.

Our previous work<sup>5</sup> indicates that it should be possible to compare the relative proton-donating powers of two XH bonds by a study of their spectroscopic behaviour in different solvents. Relative frequency shifts ( $\Delta\nu/\nu$ ) are determined for a range of solvents for the two bonds under consideration. A plot of the values of  $\Delta\nu/\nu$  of one acid against the corresponding values for the other acid is linear and has a slope related to the proton-donating powers of the two bonds.

This method is useful in that it enables a comparison to be made of proton-donating powers in non-aqueous solvents, and in particular the comparison of isotopically substituted molecules.

Consequently the monomeric OH and OD stretching frequencies of a series of acids have been measured in a range of solvents (see Table 1). The results for the aliphatic carboxylic acids are shown to be related to the  $pK$  values of these acids.

Comparison of the  $\Delta\nu/\nu$  values of [H]- and [D]-acids are also of interest in connection with Buckingham's theoretical work,<sup>6</sup> although strictly this relates only to diatomic molecules. The only measurements of this kind so far reported are those of Caldow and Thompson<sup>7</sup> on hydrogen cyanide and deuterium cyanide; they found the  $\Delta\nu/\nu$  ratios

<sup>1</sup> McDougall and Long, *J. Phys. Chem.*, 1962, **66**, 429.

<sup>2</sup> Högfeldt and Bigeleisen, *J. Amer. Chem. Soc.*, 1960, **82**, 15.

<sup>3</sup> Halpern, *J. Chem. Phys.*, 1935, **4**, 456; Wiberg, *Chem. Rev.*, 1955, **55**, 713.

<sup>4</sup> Bunton and Shiner, *J. Amer. Chem. Soc.*, 1961, **83**, 42.

<sup>5</sup> Bellamy, Hallam, and Williams, *Trans. Faraday Soc.*, 1958, **54**, 1120.

<sup>6</sup> Buckingham, *Proc. Roy. Soc.*, 1960, *A*, **255**, 32; *Trans. Faraday Soc.*, 1960, **56**, 753.

<sup>7</sup> Caldow and Thompson, *Proc. Roy. Soc.*, 1960, *A*, **254**, 1.

TABLE I.

Stretching frequencies,  $\nu_{\text{OH}}$ ,  $\nu_{\text{OD}}$  (cm.<sup>-1</sup>) for acids in various solvents.

Solvent	CCl <sub>3</sub> ·CO <sub>2</sub> H		CHCl <sub>2</sub> ·CO <sub>2</sub> H		CH <sub>2</sub> Cl·CO <sub>2</sub> H		H·CO <sub>2</sub> H		Ph·CH <sub>2</sub> ·CO <sub>2</sub> H		AcOH		Bu <sup>t</sup> ·CO <sub>2</sub> H	
	$\nu_{\text{OH}}$	$\nu_{\text{OD}}$	$\nu_{\text{OH}}$	$\nu_{\text{OD}}$	$\nu_{\text{OH}}$	$\nu_{\text{OD}}$	$\nu_{\text{OH}}$	$\nu_{\text{OD}}$	$\nu_{\text{OH}}$	$\nu_{\text{OD}}$	$\nu_{\text{OH}}$	$\nu_{\text{OD}}$	$\nu_{\text{OH}}$	$\nu_{\text{OD}}$
(Vapour) .....	3583	2641	3585	2640	3584	2640	3570	2637	3581	2642	3584	2643	3580	2641
CCl <sub>4</sub> .....	3508	2595	3518	2597	3527	2602	3518	2599	3533	2612	3539	2614	3536	2610
CS <sub>2</sub> .....	3478	2579	3492	2577	3502	2586	3495	2580	3514	2599	3520	2602	3521	2600
C <sub>6</sub> H <sub>6</sub> .....	3389	2513	3414	2529	3441	2548	3444	2553	3479	2559	3469	2570	3466	2569
$\psi$ -Cumene .....	3340	2481	3366	2499	3401	2516	3410	2527	3426	2539	3435	2548	3430	2555
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (CO <sub>2</sub> Me) <sub>2</sub> .....	3122	2340	3172	2394	3245	2430	3279	2442	3307	2457	3323	2472	3318	2473
MeOBz .....	3074	2324	3159	2367	3223	2410	3253	2427	3283	2445	3305	2452	3297	2457
MeCN .....	2273	3105	2339	3191	2386	3222	2402	3249	2422	3276	2437	3273	2439	
COMe <sub>2</sub> .....	2912	2208	2976	2237	3043	2294	3098	2321	3159	2352	3180	2370	3178	2374
Et <sub>2</sub> O .....		2196		2225		2276		2299	3093	2323	3125	2341	3145	2334

not to be identical in the two series. However, in this case the strong coupling between  $\nu_{\text{CD}}$  and  $\nu_{\text{CN}}$  might be expected to give rise to abnormalities.

In addition to the relative shifts, the ratio  $\nu_{\text{OH}} : \nu_{\text{OD}}$  is also of interest as extremely low values of this have been shown<sup>8</sup> to occur in special situations involving the likelihood of proton transfer. The present cases would be expected to be typical of more normal systems.

*Experimental.*—Spectra were measured on a Grubb-Parsons GS2 double-beam spectrometer fitted with an N.P.L.2400 line/in. replica grating. Solvent absorption was cancelled by compensation in the reference beam. The measurement of frequency is believed accurate to  $\pm 2$  cm.<sup>-1</sup>. Solvents were dried and redistilled and measurements in solution made at concentrations  $\leq 0.01\text{M}$ . Even so, dimeric (or polymeric) forms predominated in all except the most polar solvents and the monomeric bands were identified by dilution. Although in most cases no confusion existed, the combination of highly polar solvents and strong acids gave rise to ambiguous assignments and a few of these were therefore disregarded. However, in all cases sufficient results were available for satisfactory  $\Delta\nu/\nu$  plots.

The use of chloroform as a solvent was abandoned: it led to anomalous values probably attributable to its alternative function as a proton donor.

*Results and Discussion.*—*Relation between frequency shifts and pK<sub>a</sub>.* Surprisingly, it was found (as Table I shows) that  $\nu_{\text{OH}}$  for the vapour was essentially constant for the aliphatic carboxylic acids (except formic acid) at 3584 cm.<sup>-1</sup> and  $\nu_{\text{OD}}$  similarly so at 2641 cm.<sup>-1</sup>.

For the aliphatic acids  $\Delta\nu/\nu$  was plotted against the corresponding values for acetic [H]-acid as reference, and good straight lines were obtained (Fig. 1).<sup>\*</sup> The slopes of these lines should be a function of the proton-donating power of the acids relative to that of acetic acid. Although the slopes measured here would not necessarily be expected to be related to relative acidities in aqueous solutions, Goulden's observation<sup>9</sup> that  $\nu_{\text{OH}}$  for alkanolic acids in carbon tetrachloride was linearly related to pK<sub>a</sub> for the acid seems to indicate a connection, particularly as the present observations include measurements in more polar solvents and the slopes represent the average effect of a number of solvents. Consequently the slopes for the [H]-acids shown were plotted against pK<sub>H</sub> in Fig. 2. The relation is linear.

In a similar manner it is found that the relative frequency shifts  $\Delta\nu/\nu$  for the [D]-acids are linearly related to those for acetic [H]-acid or acetic [D]-acid, thus giving an indication of the effective relative acidities in non-aqueous solvents.

<sup>\*</sup> This plot indicates a relation of the form  $\Delta\nu_{\text{H}}/\nu_{\text{H}}^{\text{V}} = m \cdot \Delta\nu_{\text{X}}/\nu_{\text{X}}^{\text{V}}$ , where  $\Delta\nu = \nu^{\text{V}} - \nu^{\text{S}}$ , superscripts V and S refer to vapour and solvent, respectively, and subscripts H and X refer to the [H]-acid and reference acid, respectively. Although this plot is most convenient for illustrative purposes, an equivalent one involving less calculation is  $\nu_{\text{H}}^{\text{S}} = (m \cdot \nu_{\text{X}}^{\text{S}} \nu_{\text{H}}^{\text{V}}/\nu_{\text{X}}^{\text{V}}) + (1 - m)\nu_{\text{H}}^{\text{V}}$ . A relation of this type is also useful when comparing relative shifts for [H]- and [D]-acids.

<sup>8</sup> Bellamy and Rogasch, *Proc. Roy. Soc., A*, 1960, **A**, 257, 98.

<sup>9</sup> Goulden, *Spectrochim. Acta*, 1954, **6**, 129.

With acetic [D]-acid as reference and available values of  $pK_D$  a plot for the [D]-acids is obtained as in Fig. 2; a straight-line relation, analogous to that found for the [H]-acids, is indicated. There seems to be no reason why this could not be used to obtain values of  $pK_D$  for alkanic acids from spectroscopic measurements.

FIG. 1. Plots of  $\Delta\nu/\nu$  for acetic acid against those for (A)  $\text{CCl}_3\cdot\text{CO}_2\text{H}$ , (B)  $\text{CHCl}_2\cdot\text{CO}_2\text{H}$ , (C)  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ , (D)  $\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and (E)  $\text{Bu}^t\cdot\text{CO}_2\text{H}$  and the carboxy-deuterated analogues.

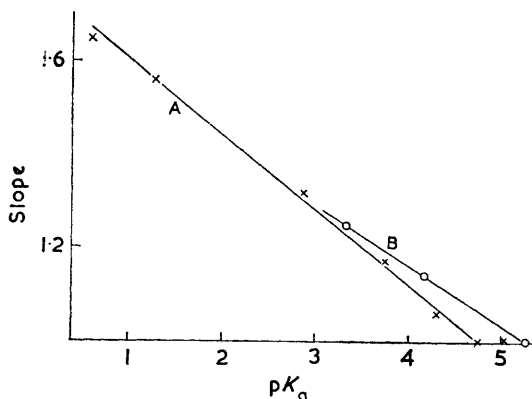
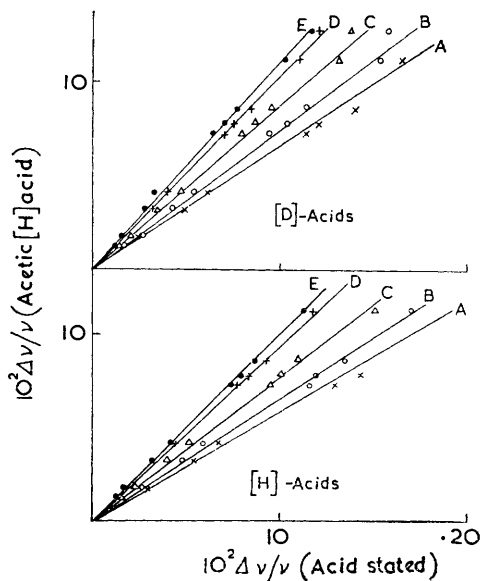


FIG. 2. Relation of the slope of plots in Fig. 1 to  $pK_a$  for (A) [H]-acids and (B) [D]-acids.

From the relations depicted in Fig. 1 it is evident, on closer inspection, that for the [H]- and the [D]-form of any one acid

$$\frac{\Delta\nu_H/\nu_H}{\Delta\nu_{HA}/\nu_{HA}} \neq \frac{\Delta\nu_D/\nu_D}{\Delta\nu_{DA}/\nu_{DA}}$$

where HA and DA refer to acetic [H]- and [D]-acid, respectively, or alternatively that the ratio

$$\frac{\Delta\nu_H/\nu_H}{\Delta\nu_D/\nu_D}$$

is not constant and equal to the value for acetic acid; the ratio indeed varies, being greatest for the strong acids trichloroacetic and dichloroacetic acid (1.15—1.16) and decreasing progressively with decreasing acid strength to a value of 1.10 for phenylacetic

acid (Table 2). This ratio is a measure of the relative acidities of the [H]- and [D]-forms of the acids in non-aqueous solvents.

TABLE 2.

Acid	$\text{CCl}_3\cdot\text{CO}_2\text{H}$	$\text{CHCl}_2\cdot\text{CO}_2\text{H}$	$\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$	$\text{H}\cdot\text{CO}_2\text{H}$	AcOH	$\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$	$\text{Bu}^t\cdot\text{CO}_2\text{H}$
$\Delta\nu/\Delta\nu_{\text{H}}/\Delta\nu/\nu_{\text{D}}$	1.15	1.16	1.14	1.11	1.11	1.10	1.12

*Frequency Shifts.*—The constancy of the  $\nu_{\text{OH}}$  and  $\nu_{\text{OD}}$  values of the acids in the vapour state has been noted above. It has previously been supposed that the OH stretching force constant in alkanolic acids was determined by the inductive properties of the substituent groups. It now appears that in the free state this is not so and that they all have essentially the same force constant. However, when the acid is placed in an environment in which association is possible, the influence of the substituent group becomes an important factor in determining the strength of the hydrogen bond formed. The fact that the  $\nu_{\text{OH}}$  frequencies in carbon tetrachloride differ and reflect the  $pK$  values in just the same way

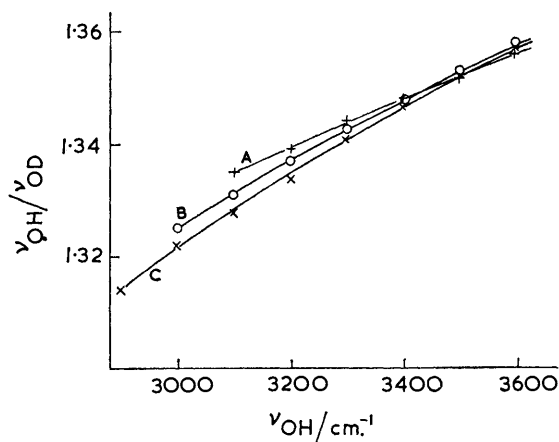


FIG. 3. Relation between  $\nu_{\text{OH}}/\nu_{\text{OD}}$  and  $\nu_{\text{OH}}$ .  
(A) Acetic, (B) monochloroacetic, (C) trichloroacetic acid.

as do the frequencies in strongly polar solvents supports the earlier suggestion<sup>5</sup> that interaction effects between proton-donors and carbon tetrachloride differ in magnitude but not in kind from the interactions which occur with ethers and other strongly polar solvents.

Fig. 3 represents an idealised plot of  $\nu_{\text{OH}}/\nu_{\text{OD}}$  against  $\nu_{\text{OH}}$  for several representative acids, on the assumption that the plots in Fig. 1 are exactly linear. As a first approximation it is seen that the OD frequency is determined largely by the OH force constant, irrespective of whether the association is between a weak acid and strong acceptor or strong acid and weak acceptor. This results in the inequality  $\Delta\nu_{\text{H}}/\nu_{\text{H}}/\Delta\nu_{\text{D}}/\nu_{\text{D}} \neq 1$ . However, in addition to the overall effect there is a progressive decrease in  $\nu_{\text{OH}}/\nu_{\text{OD}}$  for a given  $\nu_{\text{OH}}$  within the carboxylic acid series and this gives rise to the slight variations observed in the value of  $\Delta\nu_{\text{H}}/\nu_{\text{H}}/\Delta\nu_{\text{D}}/\nu_{\text{D}}$ .

*Origins of the isotope effect.* As mentioned above, the differences in the slopes of the lines of any one [H]/[D]-acid pair in Fig. 1 results from the fact that the ratio of  $\nu_{\text{OH}}/\nu_{\text{OD}}$  in a solvent differs from that in the vapour state. If these ratios were equal the [H]- and the [D]-lines would have the same slope and there would be no spectroscopic isotope effect.

The  $\nu_{\text{OH}} : \nu_{\text{OD}}$  ratio in the vapour state (1.36) is less than the theoretical value, suggesting that the potential-energy curves are anharmonic; and the anharmonicity can be expected to increase as the bond is lengthened by association effects. Because the zero-point energy of the [H]-form ( $=\frac{1}{2}h\nu_{\text{OH}}$ ) is greater than that of the [D]-form and is therefore higher on the potential-energy curve, the effect of anharmonicity changes will also be greater on the

former. Any systematic increase in anharmonicity as the OH bond lengthens will therefore lead to a progressive fall in the observed  $\nu_{\text{OH}}/\nu_{\text{OD}}$  ratios and so to the observed isotope effect.

Because of the linearity evident in Fig. 1 it is probable that the variation in the isotope effect for the acids studied is closely related to changes in anharmonicity within the series. It is interesting that, if a different reference of different anharmonicity, such as  $\nu_{\text{NH}}$  of pyrrole or  $\nu_{\text{OH}}$  of water, is chosen, the resulting plots are no longer linear.

This interpretation does not exclude the possibility that real differences in the O-H(D)-X distances might arise, and indeed microwave measurements<sup>10</sup> on association in the system  $\text{CF}_3\cdot\text{CO}_2\text{H}/\text{H}\cdot\text{CO}_2\text{H}$  and the [D]-analogues indicate that the O-O distance is longer for D-bonding than for H-bonding.

It has been suggested that differences of the latter kind may occur in special situations in which there is a double potential-energy well and proton-transfer can occur,<sup>8</sup> and there is X-ray evidence<sup>11</sup> which supports this. Indeed the very large differences between the  $\nu_{\text{OH}}/\nu_{\text{OD}}$  ratios found in such cases (often as low as 1.25 at  $\nu_{\text{OH}} 2650 \text{ cm.}^{-1}$ ) compared with the values reported here support this idea.

However, further work is required on such systems, as it is possible that even these gross changes could originate in the considerable increase in anharmonicity introduced by the double minimum.

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<sup>10</sup> Costain and Srivastava, *J. Chem. Phys.*, 1961, **35**, 1903.

<sup>11</sup> Ubbelohde and Gallagher, *Acta Cryst.*, 1955, **8**, 71.

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