689. *Hydrogen Isotope Effects in the Equilibria between 2,4-Dinitrophenol and Amines.*

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Spectrophotometric measurements show that in toluene solution triethylamine forms only hydrogen-bonded complexes with *m*-nitrophenol, *p*-nitrophenol, pentachlorophenol, and 2-bromo-5-nitrophenol, while proton transfer to give ion-pairs takes place with *o*-nitrophenol and with 2,4-, 2,5-, and 2,6-dinitrophenol. The deuterium isotope effect has been studied in toluene or chlorobenzene solution for the equilibria of 2,4-dinitrophenol with triethylamine, piperidine, pyridine, and *NN*-dimethylaniline. There is no detectable effect with triethylamine and piperidine, but with pyridine $K_H/K_D = 1{\cdot}40 \pm 0{\cdot}05$; *NN*-dimethylaniline probably occupies an intermediate position. The results can be accounted for quantitatively in terms of observed spectral frequencies and the occurrence of hydrogen bonding in the ion-pairs formed from weak bases.

MOST studies of deuterium isotope effects on equilibria have been carried out for aqueous solutions and have involved compounds which can exchange hydrogen with the solvent. This applies in particular to the growing amount of information available for isotope effects in acid–base dissociation equilibria. Under these conditions the isotopic substitution is necessarily accompanied by a change of solvent from H_2O to D_2O, and a large part of the observed isotope effect is concerned with the hydrogen-bonding with the solvent, as shown in recent papers by Bunton and Shiner.[1] The situation should be simpler for acid–base equilibria in non-exchanging solvents, such as are described in the present paper. It was at first hoped to use solvents of high dielectric constant, in which ion association could be neglected, but attempts to use dimethylformamide (ε 37) and dimethyl sulphoxide (ε 49) failed: the basic properties of the solvents themselves, and of small quantities of impurities, made it impossible to obtain accurate equilibrium constants. The final measurements were therefore made in toluene (ε 2·4) and chlorobenzene (ε 5·6), in both of which the dissociation of ion pairs should be negligible down to 10^{-4}M, so that the equilibrium constant for the reaction of an uncharged acid HB, with an uncharged base B_2 has the form $K = [B_1^-,HB_2^+]/[HB_1][B_2]$. This form of expression has in fact been found to apply to a number of acid–base equilibria in solvents of low dielectric constant.[2-6]

EXPERIMENTAL

" AnalaR " toluene was dried over sodium wire. Chlorobenzene was fractionally distilled, only the middle fraction, b. p. 131°/760 mm., being retained, and it was allowed to stand over Drierite overnight before use. Deuterium oxide was supplied by the General Dynamics Corporation, California, and was stated to contain 99·5% of D_2O.

2,5- and 2,6-Dinitrophenol were laboratory-grade preparations, supplied damp, and were dried in a vacuum-desiccator over silica gel. 2-Bromo-5-nitrophenol and pentachlorophenol had been previously prepared in this laboratory. *m*- and *p*-Nitrophenol were used as supplied without further purification. In order to obtain 3,5-dinitrophenol, 3,5-dinitroanisole was first prepared by treating 1,3,5-trinitrobenzene with sodium methoxide, following either the directions of Lobry de Bruyn[7] or those of Holleman.[8] The dinitroanisole was then

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[1] Bunton and Shiner, *J. Amer. Chem. Soc.*, 1961, **83**, 42.
[2] Bell and Bayles, *J.*, 1952, 1518.
[3] Pearson and Vogelsong, *J. Amer. Chem. Soc.*, 1958, **80**, 1038.
[4] Bayles and Chetwyn, *J.*, 1958, 2328.
[5] Bayles and Taylor, *J.*, 1961, 417.
[6] Davis *et al.*, *J. Res. Nat. Bur. Stand.*, 1951, **46**, 496; 1952, **48**, 381; 1958, **60**, 569; *J. Amer. Chem. Soc.*, 1960, **82**, 5081.
[7] Lobry de Bruyn, *Rec. Trav. chim.*, 1890, **9**, 209.
[8] Holleman, *Rec. Trav. chim.*, 1902, **21**, 432.

demethylated as described by Sidgwick and Taylor,[9] recrystallized as dihydrate from very dilute hydrochloric acid, dried at 60° for 4 hr., and recrystallized from benzene–cyclohexane. 2,4-Dinitrophenol, with which all the measurements of isotope effects were made, was recrystallized four times.

Laboratory-grade triethylamine was purified by Davis and Paaro's method.[10] It was then fractionally distilled twice, the distillate being dried over potassium hydroxide at each stage. It was stored over metallic sodium and re-distilled if it became discoloured. "AnalaR" pyridine was dried (KOH) and distilled. It rapidly discoloured in contact with sodium and was therefore stored over anhydrous calcium sulphate. Piperidine was twice fractionally distilled; it had a faint yellow colour, but its absorption was negligible at the concentrations and wavelengths used in the measurements.

Solutions were made up by weight, and concentrations converted into moles/l. by using measured densities. The preparation of deuterated solutions will be described below. Optical densities were measured with a Unicam S.P. 500 spectrophotometer with its cell compartment controlled at 25° ± 0·1°, 1 cm. matched silica cells being used.

Studies of infrared spectra of solutions in carbon tetrachloride and chloroform showed that interaction between carboxylic acids and amines gave rise to two distinct types of product depending on the nature of the acid and the base.[11, 12] One of these was a hydrogen-bonded complex $-O-H\cdots N$, with the proton still attached to oxygen, while in the other an ion pair was formed by proton transfer to nitrogen $-O^-\cdots H-N^+$, with hydrogen bonding to the oxygen. We therefore first investigated the effect of added amine on the ultraviolet spectra of a number of phenols in toluene solution. This is always to shift the main absorption to higher frequencies, and the magnitude of the shift ($\Delta\nu$) can be compared with that in aqueous solution, where there can be no doubt that the phenoxide anion is formed. The results obtained are given in Table 1. In toluene solution the base used was triethylamine, and in aqueous solution sodium hydroxide.

TABLE 1.

Effect of an excess of base on the absorption maxima of phenols.

	$\Delta\nu$ (cm.$^{-1}$)			$\Delta\nu$ (cm.$^{-1}$)	
Phenol	Toluene	Water	Phenol	Toluene	Water
m-Nitrophenol	1250	4000	*o*-Nitrophenol	4550	4800
Pentachlorophenol	1400	—	2,5-Dinitrophenol	5250	5550
p-Nitrophenol	1900	6250	2,6-Dinitrophenol	5350	5100
2-Bromo-5-nitrophenol ...	2600	8600			

With the first four phenols in Table 1 the shift of the maximum in toluene solution is much smaller than in water, and it can be concluded that no proton transfer has taken place; the relatively small shifts observed can be attributed to hydrogen bonding between the hydroxyl group and the nitrogen atom. The last three phenols in the Table exhibit a shift in toluene which is very similar to that in water, indicating that in these systems a proton transfer takes place in both solvents. 2,4-Dinitrophenol, with which all the subsequent measurements were made, also belongs to the second class. The spectra both in presence and absence of base are more complicated, having several maxima, but (as already demonstrated by Bayles and Chetwyn [4] and Bayles and Taylor [5] in other non-aqueous solvents) the spectrum in toluene in presence of an excess of triethylamine resembles closely that of the free anion in water. 3,5-Dinitrophenol shows a shift of the main peak of 2300 cm.$^{-1}$, but also the appearance of a weak maximum shifted by 5400 cm.$^{-1}$. Since the shift on forming the anion in aqueous solution is 4600 cm.$^{-1}$, it is probable that the toluene solutions contain both types of complex, those with hydrogen bonds predominating.

Equilibrium constants for 2,4-dinitrophenol–triethylamine in toluene were determined by measuring optical densities at 400 mμ. In the absence of base, $\varepsilon_1 = 102$; and with an excess of triethylamine (0·1—0·3M), $\varepsilon_2 = 8130$. In solutions containing less triethylamine the ratio $[B_1^-,HB_2^+]/[HB_1] = r$ is then $(E - 102c_A)/(8130c_A - E)$, where E is the observed extinction coefficient and c_A the total concentration of dinitrophenol. The equilibrium constant (see

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[9] Sidgwick and Taylor, *J.*, 1922, **121**, 1853.

[10] Davis and Paaro, *J. Amer. Chem. Soc.*, 1960, **82**, 5081.

[11] Barrow and Yerger, *J. Amer. Chem. Soc.*, 1954, **76**, 5212.

[12] Barrow, *J. Amer. Chem. Soc.*, 1956, **78**, 5082.

above) is then given by $K = r(r + 1)/\{c_B(r + 1) - c_A r\}$, where c_B is the total concentration of base. Measurements were made with $c_A = 0{\cdot}8$—3×10^{-4}, $c_B = 10^{-4}$—10^{-3}, $r = 0{\cdot}16$—$1{\cdot}7$. There were no systematic variations in K, and the mean value for 9 experiments was $K_H = 2110 \pm 90$. A similar set of experiments was carried out in which the solutions had been saturated with water, the value of c_A in the final solution being determined by adding an excess of triethylamine and measuring the optical density. The mean value for 18 experiments was $K_H = 2110 \pm 30$, identical with that for dry toluene.

The fact that the equilibrium constant is unaffected by saturating the solution with water greatly facilitates the study of the deuterated phenol, since it is possible to work with solutions saturated with deuterium oxide, thus preventing re-protonation by traces of moisture. The mean of 12 experiments gave $K_D = 2070 \pm 30$; *i.e.*, there is no detectable isotope effect in this system.

The system 2,4-dinitrophenol–pyridine could not be studied in toluene because of the low solubility of the salt formed. Measurements were possible in chlorobenzene solution, but even with high concentrations of pyridine only a small proportion of the phenol is converted into the basic form. The composite absorption curve showed that the product had an absorption maximum close to 400 mμ, thus characterizing it as an ion pair, but it was not possible to determine its extinction coefficient directly. However, if $r \ll 1$ and $c_B \gg c_A$, then $K = r/c_B = R/\varepsilon_2$, where $R = (E - \varepsilon_1 c_A)c_A c_B$ and ε_1 and ε_2 are the extinction coefficients of the nitrophenol and the ion pair, respectively. In determining the isotope effect we then have $K_H/K_D = R_H/R_D$, involving now only measurable quantities.

Measurements were made with c_A about 7×10^{-4}M and $c_B = 0{\cdot}3$—$0{\cdot}4$M. In these solutions $r = 0{\cdot}03$—$0{\cdot}04$, so that the above approximations are justified. Solutions were saturated with water or deuterium oxide. Since chlorobenzene and deuterium oxide have almost the same density, settling is very slow: this was cured by shaking the solutions with a little solid sodium chloride, previously dried at 150°, which increases the density of the aqueous phase. The mean of 7 experiments for each isotope gave $R_H = 1010 \pm 30$, $R_D = 723 \pm 12$, and hence a considerable isotope effect, namely, $K_H/K_D = R_H/R_D = 1{\cdot}40 \pm 0{\cdot}05$. If it is assumed that ε_2 has the same value as in the 2,4-dinitrophenol–triethylamine system, then $K_H = 0{\cdot}102$, and $K_D = 0{\cdot}073$, but these values are less reliable than their ratio.

Attempts were made to measure the isotope effect directly by observing the change in optical density occurring when a deuterated solution of phenol and amine was shaken with crystals of sodium sulphate decahydrate, which should replace the deuterium by hydrogen. Successive experiments gave $K_H/K_D = 1{\cdot}38, 1{\cdot}27, 1{\cdot}31, 1{\cdot}38, 1{\cdot}29$ (mean $1{\cdot}33 \pm 0{\cdot}02$). This value is probably less reliable than that given above, since there is some evidence that isotopic exchange is slow and that dinitrophenol may be absorbed on the surface of the crystals.

The system 2,4-dinitrophenol–piperidine was studied in chlorobenzene by the method used for triethylamine. Both components were present at 1—2×10^{-4}M, and r varied between 0·6 and 1·0. The mean of four experiments with each isotope gave $K_H = 3970 \pm 30$, $K_D = 3970 \pm 50$, and hence no measurable isotope effect.

Preliminary measurements with 2,4-dinitrophenol–*NN*-dimethylaniline in chlorobenzene were made by the method used for pyridine, with 0·47M-amine and $3{\cdot}4 \times 10^{-3}$M-phenol. Two concordant experiments with each isotope gave $R_H = 257$, $R_D = 231$, $K_H/K_D = R_H/R_D = 1{\cdot}12$. The assumption that ε_2 has the same value as in the triethylamine system gives $K_H = 0{\cdot}026$, $K_D = 0{\cdot}023$.

DISCUSSION

Since solvent isotope effects are absent in the systems studied, the main source of a hydrogen isotope effect in the phenol–amine equilibria will lie in a change of the hydrogen-stretching frequency between O–H and N$^+$–H. Fortunately the relevant frequencies can be estimated closely from recent experimental data. Cardinaud[13] gives $\nu_H = 3240$ cm.$^{-1}$, $\nu_H/\nu_D = 1{\cdot}33$, for O–H stretching for *o*-nitrophenols in benzene. Nuttall, Sharp, and Waddington[14] studied the infrared spectra of solid trimethylammonium and pyridinium salts. They found that the N–H stretching frequencies fell into two classes, according to whether hydrogen bonding to the anion was present (as with halides) or

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[13] Cardinaud, *Bull. Soc. chim. France*, 1960, 34.

[14] Nuttall, Sharp, and Waddington, *J.*, 1960, 4965.

absent (as with perchlorates and tetrafluoroborates). Their average values are given in Table 2. If these values are applicable to our measurements with 2,4-dinitrophenol

TABLE 2.

N–H stretching frequencies (cm.$^{-1}$) in amine salts.

	Trimethylammonium	Pyridinium
Hydrogen-bonded	$\nu_H = 2730$	2700
Not hydrogen-bonded	$\nu_H = 3180$	3240
$\nu_H/\nu_D =$	1·33	1·32

we see that in the absence of hydrogen bonding the formation of the ion pair leads to very little change of frequency, and hence a negligible isotope effect, as was found experimentally for reaction with triethylamine and piperidine. On the other hand, for a hydrogen-bonded ion-pair there is a considerable change of frequency, and the standard equations for isotope effects [15] give $K_H/K_D = 1{\cdot}37$ if the frequency for pyridinium salts is used and it is assumed that no other frequencies are affected by isotopic substitution; this is close to the observed value of $1{\cdot}40 \pm 0{\cdot}05$. Our experimental results can therefore be accounted for theoretically if it is assumed that the ion pairs formed from dinitrophenol and pyridine are hydrogen-bonded, while those from triethylamine or piperidine are not. This is consistent with the stronger binding of the proton to the nitrogen by the two stronger bases. The provisional results obtained for *NN*-dimethylaniline suggest that it is intermediate between the two extremes. The absorption maximum is a broad one and might conceal absorption by two different species. Although *NN*-dimethylaniline is a weak base, like pyridine, hydrogen bonding with the phenoxide oxygen would be rendered more difficult by the steric repulsion of the methyl groups.

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[*Received, April 3rd,* 1962.]

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[15] See, *e.g.*, Bigeleisen and Mayer, *J. Chem. Phys.*, 1947, **15**, 261.