291. *The Dissociation Constants of Some Nitrophenols in Deuterium Oxide.*

By D. C. Martin and J. A. V. Butler.

A spectrophotometric method has been used to determine the relative dissociation constants of some nitrophenols in H_2O and D_2O. It is found that the ratio K_h/K_d increases as K_h decreases and the values found lie close to the curve given by Rule and LaMer (*J. Amer. Chem. Soc.*, 1938, **60**, 1974). The ratio appears to be appreciably higher in compounds having nitro-groups only in the *m*-position.

It has been found (Lewis and Schutz, *J. Amer. Chem. Soc.*, 1934, **56**, 1913) that acids in general are considerably weaker in heavy than in ordinary water. Halpern (*J. Chem. Physics*, 1935, **3**, 459) ascribed the difference to the difference of zero-point energy of the proton and deuteron in the acid, as compared with H_3O^+ and D_3O^+, and suggested that this is determined by the strength of the binding so that the ratio K_h/K_d, where K_h and K_d are the dissociation constants in H_2O and D_2O, should be greater the weaker the acid. Hornel and Butler (J., 1936, 1361) considered that the force constant was more important than the binding energy in determining the zero-point energy difference.

At the time this work was begun, the actual variation of the ratio with the strength of the acid was quite uncertain. Schwarzenbach (*Z. Elektrochem.*, 1938, **44**, 46) pointed out that an important factor was the less basic character of heavy than of light water, as a result of which, if the binding of a deuteron in the acid were the same as that of a proton, the acid would be weaker in the former than in the latter by a factor of about 2.

The values quoted by Schwarzenbach show very little evidence of any definite trend of K_h/K_d with the strength of the acid. LaMer and his collaborators (Korman and LaMer,

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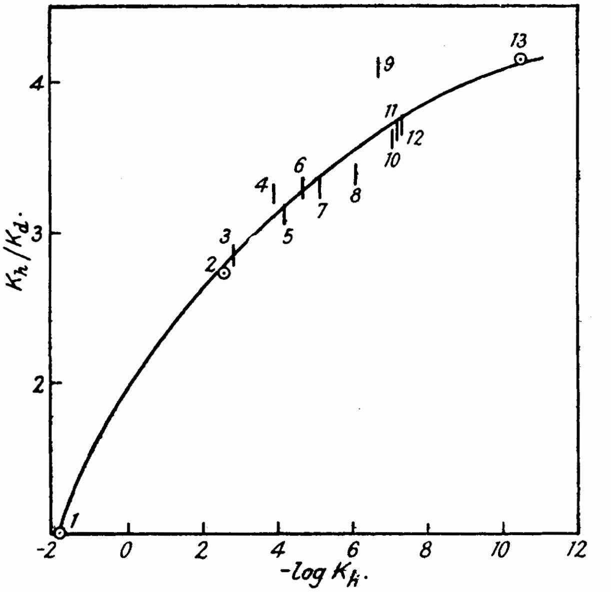
* The statement that amphiporine gives a picrate crystallising in needles (Bacq, *loc. cit.*) is incorrect, and was made on the basis of the present writer's observations. The material available at that time was extremely minute, and the observed needles were no doubt sodium picrate.

J. Amer. Chem. Soc., 1936, **58**, 1396; Rule and LaMer, *ibid.*, 1938, **60**, 1974) have, however, since made a number of accurate measurements, which indicate a steady increase of the ratio K_h/K_d as the strength of the acid decreases.

In this work we have examined a number of nitrophenols, which are very suitable for this purpose because (1) a considerable range of acidity can be obtained according to the number and position of the substituent nitro-groups; (2) their colour permits the use of a spectrophotometric method.

The method is a comparison of the extent of the dissociation of the nitrophenol in buffer solutions of known composition in light and in heavy water. It is necessary that the relative dissociation constants of the buffer acid in the two solvents should be known. The only buffers suitable for this purpose were those prepared from phosphoric (second stage) and acetic acids. Originally the ratios for those derived from dihydrogen phosphate and acetic acid (Schwarzenbach, Epprecht, and Erlenmeyer, *Helv. Chim. Acta*, 1936, **19**, 1292) were employed, but the results have been recalculated using Rule and LaMer's more recent data (*loc. cit.*).



The results are given in the following table together with some previous determinations, and the figure shows K_h/K_d plotted against log K_h. It can be seen that the points agree quite well with LaMer and Rule's curve, except that for 3 : 5-dinitrophenol.

No. in fig.	Acid.	$-\log K_h$.	K_h/K_d.	No. in fig.	Acid.	$-\log K_h$.	K_h/K_d.
1	H_3O^+	$-1{\cdot}74$	(1)	8	Bromothymol-blue	6·15	$3{\cdot}4_0$
2	Chloroacetic acid	2·76	2·74*	9	3 : 5-Dinitrophenol	6·70	$4{\cdot}1_1$
3	2 : 6-Dinitrophenol	3·58	$2{\cdot}8_4$	10	$H_2PO_4^-$	7·19	3·62‡
4	2 : 4- ,,	4·02	$3{\cdot}2_8$	11	*p*-Nitrophenol	7·24	$3{\cdot}6_7$
5	Benzoic acid	4·21	3·13‡	12	*o*- ,,	7·25	$3{\cdot}7_1$
6	Acetic ,,	4·74	3·33†	13	Quinol	10·58	4·16‡
7	2 : 5-Dinitrophenol	5·17	$3{\cdot}3_2$				

* Lewis and Schutz, *loc. cit.* † Korman and LaMer, *loc. cit.* ‡ Rule and LaMer, *loc. cit.*

The dissociation constant of *m*-nitrophenol is unfavourably placed with reference to these buffer solutions and an accurate ratio could not be obtained, but the values noted were also distinctly high, and it appears possible that in the acids containing nitro-groups only in the *m*-position the ratio is distinctly higher than corresponds to the same K_h in the other compounds.

Measurements were also made with a typical colorimetric indicator, *viz.*, bromothymol-blue. The behaviour of this fitted in with that of the other substances and its dissociation in a given buffer in deuterium oxide differs little from its dissociation in a buffer of the same composition in ordinary water.

EXPERIMENTAL.

The method was the spectrophotometric determination of the dissociation of the nitrophenol in similar buffers in H_2O and 99% D_2O. If K_{HA} is the thermodynamic dissociation constant of the substance investigated and K_{HB} that of the acid used for the buffer solutions, we have

$$K_{HA}/K_{HB} = (C_{HB}C_{A^-}/C_{HA}C_{B^-})(f_{HB}f_{A^-}/f_{HA}f_{B^-})$$

where the C terms are concentrations and the f terms are the activity coefficients. If the acids HB and HA are of the same ionic type, then the ratio $f_{HB}f_{A^-}/f_{HA}f_{B^-}$ does not differ greatly from unity in dilute solutions. Since we are only concerned with a comparison of equally concentrated solutions in H_2O and D_2O, we shall assume that the ratio $\Sigma f_{H_2O}/\Sigma f_{D_2O}$ does not differ appreciably from unity, not only in acetate buffers, but also in the case of the phosphate buffers which we were obliged to use.

If

$$(C_{HB}/C_{B^-})_{H_2O} = (C_{DB}/C_{B^-})_{D_2O}$$

we have

$$K_{HA,H_2O}/K_{DA,D_2O} = (K_{HB,H_2O}/K_{DB,D_2O})(C_{A^-}/C_{HA})_{H_2O}(C_{DA}/C_{A^-})_{D_2O}$$

or

$$\log \frac{K_{HA,H_2O}}{K_{DA,D_2O}} = \log \frac{K_{HB,H_2O}}{K_{DB,D_2O}} + \log \frac{(C_{A^-}/C_{HA})_{H_2O}}{(C_{A^-}/C_{DA})_{D_2O}}$$

The measurements were made in the following way. (*a*) The buffer solutions were prepared and very small quantities of the nitrophenol added. The absorption spectra of the nitrophenols begin at about 4700 A, and it was found convenient to measure the absorption at 4500 A. The absorption coefficient was measured by using a Hilger–Nutting wave-length spectrophotometer for the visible region. This measurement (d') is proportional to the concentration of anion A^- present in the solution at the p_H determined by the composition of the buffer. (*b*) A very small quantity of concentrated sodium hydroxide (0·01 ml. of 8N-NaOH), sufficient to convert the nitrophenol completely into its alkaline form, was then added, and a second measurement (d'') made. It was found that further additions of alkali caused no change in the absorption coefficient, and therefore d'' is a measure of the concentration of the anion A^- at complete dissociation.

The measurements were carried out at room temperature (18° ± 2°). Every reading is the average of 10 settings, and the zero of the instrument was checked before each set of readings.

Materials.—The nitrophenols were obtained from British Drug Houses, Ltd., and purified by several recrystallisations, except 3 : 5-dinitrophenol; after much difficulty, this was prepared as follows. Trinitrobenzene ("Organic Syntheses," Vol. II, 93) was converted into 3 : 5-dinitroanisole by keeping 10 g. of it in a flask for 2 days with 1·5 g. of sodium in 100 ml. of methyl alcohol. The needle-shaped crystals which separated (yield 90%), m. p. 105° (Holleman and Wilhemy, *Rec. Trav. chim.*, **1902**, **21**, 432) were hydrolysed by heating with 4—5 mols. of concentrated sulphuric acid in an open vessel at 130° for 6 hours. Water was added, and the resulting solution extracted with ether. A yellowish impure substance obtained on evaporating the ether was crystallised from dilute hydrochloric acid (m. p. 56—57°). This, which appeared to be a hydrate, was dried over phosphoric oxide in a vacuum desiccator and then melted sharply at 124°.

The following buffer constants were assumed (Rule and LaMer, *loc. cit.*) :

Acid	$CH_3{\cdot}CO_2H$	$H_2PO_4^-$
$\log K_h/K_d$	0·522	0·559

where $K_h/K_d = K_{HA,H_2O}/K_{DA,D_2O}$

The measurements are given in the following tables. Similar measurements were also made with the indicator bromothymol-blue. The dissociation constant of *m*-nitrophenol is unfavourably placed for these buffers and only an approximate value could be obtained. In these tables a revision has been made to correspond to Rule and LaMer's values, and these are given in the last column which has also been corrected to correspond to 100% D_2O.

Acetate buffers.

Substance.	Solvent.	$\log \frac{[HAc]}{[NaAc]}$.	$d'/(d'' - d')$.	K_h/K_d. Found.	K_h/K_d. Corr. to 100% D_2O.
2 : 6-Dinitrophenol	D_2O	1·000	1·928	$2{\cdot}8_1$	$2{\cdot}8_4$
	H_2O	1·000	1·625		
2 : 4- ,,	D_2O	$\bar{1}{\cdot}1746$	0·754	$3{\cdot}2_2$	$3{\cdot}2_8$
	H_2O	$\bar{1}{\cdot}1746$	0·729		
2 : 5- ,,	D_2O	0·6218	1·447	$3{\cdot}2_6$*	$3{\cdot}3_2$
	H_2O	0·6218	1·418		

Phosphate buffers.

Substance.	Solvent.	$\log \frac{[Na_2HPO_4]}{[KH_2PO_4]}$.	$\frac{d'}{d'' - d'}$.	K_h/K_d. Found.	K_h/K_d. Corr. to 100% D_2O.
o-Nitrophenol	D_2O	0·000	0·578	$3{\cdot}6_9$	$3{\cdot}7_1$
	H_2O	0·000	0·586		
p-Nitrophenol	D_2O	0·000	0·738	$3{\cdot}6_4$	$3{\cdot}6_7$
	H_2O	0·000	0·744		
m-Nitrophenol	D_2O	0·687	0·191	$3{\cdot}9_8$	$4{\cdot}0_0$
	H_2O	0·687	0·209		
	D_2O	0·710	0·175	$3{\cdot}8_1$	$3{\cdot}8_3$
	H_2O	0·710	0·184		
	D_2O	0·798	0·177	$4{\cdot}1_4$	$4{\cdot}1_8$
	H_2O	0·798	0·198		
	D_2O	0·847	0·222	$4{\cdot}3_6$	$4{\cdot}3_8$
	H_2O	0·847	0·267		
	D_2O	1·064	0·220	$5{\cdot}0_9$	$5{\cdot}1_1$
	H_2O	1·064	0·309		
3 : 5-Dinitrophenol	D_2O	$\bar{1}{\cdot}9620$	1·636	$4{\cdot}1_4$	$4{\cdot}1_6$
	H_2O	$\bar{1}{\cdot}9620$	1·871		
	D_2O	0·0071	1·523	$3{\cdot}7_9$	$3{\cdot}8_1$
	H_2O	0·0071	1·593		
	D_2O	0·0216	1·625	$4{\cdot}1_9$	$4{\cdot}2_1$
	H_2O	0·0216	1·882		
	D_2O	0·1572	2·000	$4{\cdot}2_3$	$4{\cdot}2_5$
	H_2O	0·1572	2·333		
	D_2O	0·2693	2·339	$4{\cdot}0_9$	$4{\cdot}1_1$
	H_2O	0·2693	2·637		
Bromothymol-blue	D_2O	0·000	0·728	$3{\cdot}3_9$	$3{\cdot}4_0$
	H_2O	0·000	0·681		

We thank the D.S.I.R. for a maintenance grant (to D. C. M.), and Imperial Chemical Industries for a grant.

[*Received, July* 1*st*, 1939.]