

Dissociation Constant of 3,5-Dinitrophenol in Deuterium Oxide at 25° C.

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Using a spectrophotometric method, the dissociation constant of 3,5-dinitrophenol in deuterium oxide at 25° C. has been found to be 4.95×10^{-8} (molality scale), $pK = 7.305$. An earlier observation, that the difference between the pK value of this phenol in heavy water and in ordinary water is large compared with that found for other nitrophenols, is confirmed.

IN their early work on the relation between the dissociation constants of acids in ordinary water and in deuterium oxide, Martin and Butler (5) measured the dissociation constants of a number of nitrophenols in both solvents. If the difference in pK , $\Delta pK = pK(\text{in } D_2O) - pK(\text{in } H_2O)$, is plotted against $pK(\text{in } H_2O)$, it is found (2, 5) that there is an approximately linear increase in ΔpK with increasing value of $pK(\text{in } H_2O)$. The point for 3,5-dinitrophenol on such a plot, however, seems to be too high by as much as 0.07 in ΔpK . As the pK value of this phenol in water has been redetermined recently (6) by a spectrophotometric method, it seemed worthwhile repeating the measurements using deuterium oxide as solvent.

MATERIALS

The 3,5-dinitrophenol was a portion of that used in earlier work (6). Potassium dihydrogen phosphate and disodium hydrogen phosphate were NBS standard samples 186 Ib and 186 IIb, respectively. Sodium chloride was recrystallized once from water. The deuterium oxide contained 99.8 mole % D_2O .

METHOD

If 3,5-dinitrophenol is dissolved in a phosphate buffer solution in deuterium oxide, the dissociation equilibrium is described by the equation

$$pK = -\log a_{D^-} - \log m_{N^-}/m_{DN} - \log \gamma_{N^-}/\gamma_{DN} \quad (1)$$

where N^- and DN designate the phenolate anion and the undissociated phenol, respectively. E.m.f. measurements have yielded values of the quantity $pa_D\gamma_{Cl^-}$ ($\equiv -\log a_{D^-}\gamma_{Cl^-}$) for a number of phosphate buffer solutions, with added sodium chloride, in deuterium oxide (4). Consequently,

$$pK = pa_D\gamma_{Cl^-} - \log m_{N^-}/m_{DN} - \log \gamma_{N^-}/(\gamma_{Cl^-}\gamma_{DN}) \quad (2)$$

Since 3,5-dinitrophenol has an absorption spectrum which is markedly dependent on the acidity of the medium, we can write $m_{N^-}/m_{DN} = (D - D_1)/(D_2 - D)$. In the present work, a Cary 14 instrument was used for measurements of absorbance (optical density), the cell compartment being controlled at $25^\circ \pm 0.1^\circ C$.

RESULTS

A few measurements were made using ordinary water as solvent. These gave $pK = 6.684$, which compares with $pK = 6.692$ obtained previously (6).

The results of measurements in deuterium oxide are given in Table I. The final column gives values of pK after a correction (7) for the effect of the partially dissociated phenol on the $pa_D\gamma_{Cl^-}$ value of the buffer solution. In this

instance, the correction is comparatively large; the correction depends on the ratio of the concentration of the phenol to that of the buffer constituents. The former had to be made comparatively large because meta-substituted nitrophenols have low extinction coefficients and it was necessary to use comparatively high concentrations of phenol to obtain useful values of the absorbance.

DISCUSSION

The final value, obtained by taking the mean of the values in Table I, is $pK = 7.305$, $K = 4.95 \times 10^{-8}$ mole kg^{-1} . The standard deviation in pK is 0.008. Because the $pa_D\gamma_{Cl^-}$ values used (4) are based on the molality scale (moles per kilogram of solvent), K is also on the molality scale. Since $pK(\text{in } H_2O) = 6.692$ (6), $\Delta pK = 0.613$.

It is not clear what scale was used by Martin and Butler (5); their values resulted from the use of the equation:

$$pK = pK(\text{DB}^- \text{ in } D_2O) - pK(\text{HB}^- \text{ in } H_2O) +$$

$$\log \frac{(C_{N^-}/C_{HN})_{H_2O}}{(C_{N^-}/C_{DN})_{D_2O}} - \log \frac{(C_{B^-}/C_{HB^-})_{H_2O}}{(C_{B^-}/C_{DB^-})_{D_2O}} \quad (3)$$

where HB^- and DB^- are the acidic components of the buffer solution (in this case, either the $H_2PO_4^-$ or the

Table I. Dissociation Constant of 3,5-Dinitrophenol in Deuterium Oxide at 25° C.

I^a	$pa_D\gamma_{Cl^-}^b$	D	$\log \frac{D - D_1}{D_2 - D}$	pK	pK (cor)
Concentration of 3,5-dinitrophenol; 3.87×10^{-4} mole/liter, 3.49×10^{-4} m.					
Wavelength 410 $m\mu$; 1-cm. cell; $D_1 = 0.005$, $D_2 = 0.961$					
0.1000	7.531	0.592	0.202	7.329	7.319
0.0750	7.555	0.608	0.233	7.322	7.309
0.0500	7.590	0.626	0.268	7.322	7.302
0.0250	7.637	0.636	0.288	7.349	7.310
Concentration of 3,5-dinitrophenol; 4.53×10^{-4} mole/liter, 4.09×10^{-4} m.					
Wavelength 400 $m\mu$; 1-cm. cell; $D_1 = 0.018$, $D_2 = 1.126$					
0.0898	7.539	0.717	0.233	7.306	7.293
0.0662	7.568	0.729	0.253	7.315	7.298
0.0430	7.602	0.740	0.272	7.330	7.304
0.0208	7.654	0.752	0.293	7.361	7.307

^a Buffer solution contained equimolar (m.) mixture of potassium dihydrogen phosphate, disodium hydrogen phosphate, and sodium chloride. $I = 5m$. ^b See (4).

$D_2PO_4^-$ ion). Their solutions were made up in such a way that the last term in this equation is zero. Their experimental measurements gave values of the third term on the right-hand side of this equation; they are independent of the concentration scale used. They made five determinations of this term; their average value was 0.052 with a mean deviation from the average of ± 0.013 . The measurements were made at 18°C.; at this temperature, $pK(D_2PO_4^- \text{ in } D_2O) = 7.804$ (4) and $pK(H_2PO_4^- \text{ in } H_2O) = 7.221$ (1, 3), so that ΔpK (buffer acid) = 0.587. Hence, for dinitrophenol at 18°C., the work of Martin and Butler gives $\Delta pK = 0.639$, which compares with our value of 0.613 at 25°C.; little is known about the influence of temperature on ΔpK but ΔpK for the second stage of dissociation of phosphoric acid is 0.007 greater at 18° than at 25°C. We conclude that our results are in substantial agreement with those of Martin and Butler and that the ΔpK value for 3,5-dinitrophenol is anomalously higher than the values for other nitrophenols.

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NOMENCLATURE

- a_{D^+} = deuterium ion activity
 C_i = concentration of i species
 D_1, D_2, D = absorbances of solutions of 3,5-dinitrophenol in acid, alkaline, and buffer solutions, respectively
 I = total ionic strength
 m = molality, mole/kg.
 K = dissociation constant on molality scale, mole/kg.
 γ_i = activity coefficient (molal scale) of i species

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Vapor Pressures of Fluorine- and Silicon-Containing Derivatives of Some Hydroxylic Compounds

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The vapor pressures of the acetates, trifluoroacetates, pentafluoropropionates, and trimethylsilyl ethers of 1-butanol, cyclohexanol, *m*-cresol, and *p*-cresol, and *n*-butyl *tert*-butyl ether were measured in the 80° to 130° C. range. Antoine constants have been calculated. Where comparison is possible, the results of this work are in reasonable agreement with data reported in the literature.

IN A GAS chromatographic study of some esters and ethers of certain alcoholic and phenolic compounds, it became necessary to know vapor pressure *vs.* temperature relationships in the 80° to 130° C. range. Since the literature contained little more than a few boiling ranges, the data had to be experimentally determined. It was felt that this information would be of interest because some of the compounds are common, while others are of a hybrid chemical composition and have been rather incompletely characterized.

EXPERIMENTAL

The compounds investigated were the acetates, trifluoroacetates, pentafluoropropionates, and trimethylsilyl ethers of 1-butanol, cyclohexanol, *m*-cresol, and *p*-cresol, and also *n*-butyl *tert*-butyl ether. The parent compounds and acetates were obtained commercially and used without further purification, as were the butyl fluoroesters (Peninsular ChemResearch Corp.). Gas chromatographic analyses revealed no impurities. Other fluoroesters were made

according to Shulgin (17) using trifluoroacetic anhydride (Aldrich Chemical Co.) and pentafluoropropionic anhydride (Pierce Chemical Co.). The trimethylsilyl ethers were made using Freedman and Croitoru's (6) modification of Langer *et al.*'s hexamethyldisilazane (Aldrich) procedure (10). The *n*-butyl *tert*-butyl ether was prepared by a Williamson synthesis from sodium *tert*-butoxide (sodium hydride plus *tert*-butyl alcohol) and *n*-butyl bromide. All compounds were purified by distilling at least twice, with the center cut retained each time. Chromatographic analyses showed a minimum purity of 99.3% with the exception of the *n*-butyl *tert*-butyl ether, which had a 4% impurity of slightly higher boiling point.

Vapor pressures were determined using the ebulliometer and experimental method of Hoover *et al.* (8). A few boiling stones were needed to prevent bumping. The apparatus had to be wrapped in asbestos to prevent excessive heat loss which led to condensation in the bottom portion only. The thermometer was calibrated in a liquid bath against a National Bureau of Standards corrected thermometer. Temperatures were read to 0.1°C. with a magnifier, the