

Fig. 3. Difference spectra.  $A$  is recalculated to a concentration corresponding to  $A=1.00$  at  $17\,000\text{ cm}^{-1}$  and  $\text{pH } 7.0$ .

phosphate at  $\text{pH } 7$  and has further been carefully dialysed. Almost all the humic acid fractions obtained by pyrophosphate extraction<sup>1</sup> show similar difference spectra as the humic acid studied here, differing from those extracted with concentrated sodium hydroxide. The latter extraction thus seems to cause drastic chemical changes of the humic acids. This has been confirmed by treatment of the present humic acid with concentrated  $\text{NaOH}$  solutions. The resulting humic acid exhibits a strong  $\Delta A$  maximum at  $28\,500\text{ cm}^{-1}$  as reported earlier. The difference spectra are thus very sensitive to changes in the treatment of the soils and less suitable for characterization. The shape of the  $\log A$  curves need not vary much to give such appreciable shifts in the difference spectra.

The change in shape with  $\text{pH}$  can be found from  $\Delta \log A$  curves (Fig. 4). Such difference curves show the pronounced general effect and indicate that the most typical specific effect is obtained at  $16\,000\text{ cm}^{-1}$  in basic solution (*vide supra*). They might be more valuable for characterization of humic acids than the common difference ( $\Delta A$ ) curves.

On the basis of this study it is suggested that the shape of the  $\log A$  curve at dif-

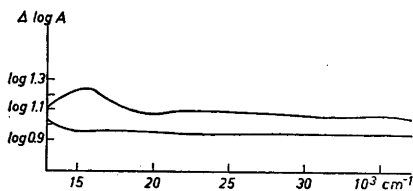


Fig. 4.  $\log A$  for  $\text{pH } 11.5$  (upper curve) and  $\text{pH } 2.0$  (lower curve) relative to  $\text{pH } 7.0$ .

ferent  $\text{pH}$  can be safely used as a characteristic if its constancy is proved by measurements at different dilutions. Difference spectra can only have a diagnostic value at present. The general and specific effects of  $\text{pH}$  variation on the absorption spectra of humic acids should be further studied.

1. Lindqvist, I. *Lantbrukshögskolans Ann.* **34** (1968) 377.
2. Lindqvist, I. and Bergman, B. *Acta Chem. Scand.* **20** (1966) 918.

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## The Protonation of Benzyl Alcohol in Aqueous Sulfuric Acid

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Branching of the hydrocarbon chain has very little effect on the basicity of aliphatic alcohols.<sup>1</sup> By Raman spectral,<sup>2</sup> extraction,<sup>1,3</sup> and solubility<sup>4</sup> studies, aliphatic alcohols, regardless of structural differences, have been found to be half-protonated in sulfuric acid solutions whose  $H_0$  values lie within the very narrow range from  $-2.2$  to  $-2.7$ . We wish to report that even a phenyl substituent has very little influence on the basicity because extraction studies carried out with benzyl alcohol revealed that this alcohol is half-protonated in  $44.6\text{ wt.}\%$  sulfuric acid, the  $H_0$  value of which is  $-2.81$ .

The solvent extraction—GLC method<sup>5</sup> used previously<sup>3</sup> was employed. Values of the ratio

$$D = \frac{[\text{ROH}]_{\text{org.}}}{([\text{ROH}]_{\text{tot.}} - [\text{ROH}]_{\text{org.}})}$$

where  $[\text{ROH}]_{\text{tot.}}$  and  $[\text{ROH}]_{\text{org.}}$  are the analytical concentrations of the alcohol in cyclohexane before and after shaking the solution with a sulfuric acid solution, were determined. The values of the ratio  $D$  for benzyl alcohol at different sulfuric acid concentrations are given in Table 1 and

Table 1. Extraction of benzyl alcohol from cyclohexane by aqueous sulfuric acid at 25°C.

[H <sub>2</sub> SO <sub>4</sub> ] mole/l	H <sub>0</sub>	D	K <sub>D</sub> (extra- polated)
0.790	-0.10	0.318	
1.468	-0.54	0.386	
1.925	-0.80	0.428	
2.375	-1.05	0.448	
2.862	-1.31	0.481	
4.579	-2.09	0.470	0.590
5.176	-2.36	0.426	0.626
5.981	-2.75	0.346	0.679
6.178	-2.86	0.295	0.693
6.781	-3.19	0.243	0.737
7.396	-3.54	0.186	0.784
8.372	-4.07	0.105	0.855
9.118	-4.46	0.051	0.908
10.00	-4.89	0.010	

plotted against H<sub>0</sub> in Fig. 1. In the range where protonation does not occur, the distribution coefficient K<sub>D</sub> of the alcohol is equal to the ratio D and varies with the acidity function H<sub>0</sub> as given by the equation

$$K_D = -0.134H_0 + 0.310$$

within the limits of experimental error. We have assumed that this equation is valid also in the range where protonation occurs. Values of K<sub>D</sub> employed in subsequent calculations are given in Table 1. The equa-

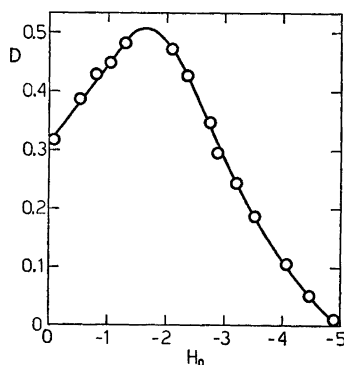


Fig. 1. Distribution ratio for benzyl alcohol between cyclohexane and aqueous sulfuric acid as a function of the acidity function H<sub>0</sub>.

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tion fitted by the method of least squares to the experimental data in the protonation range from 20 to 94 % is

$$H_0 \pm 0.07 = (1.36 \pm 0.04) \log [D/(K_D - D)] - 2.81 \pm 0.03$$

where the errors are standard deviations.

The deviation of the slope from unity may be partly due to the uncertainty of the extrapolated K<sub>D</sub> values, but it probably indicates that benzyl alcohol is not a Hammett base. It is, however, possible to compare the basicities of compounds if they follow the same acidity function.

The intercept  $-2.81 \pm 0.03$  is the H<sub>0</sub> value of the solution where benzyl alcohol is half-protonated. When compared with the H<sub>0</sub> values,  $-2.7$  and  $-2.4$ , where cyclohexylmethanol<sup>3</sup> and 1-butanol,<sup>1</sup> respectively, are half-protonated, this value implies a very slightly lower basicity. The difference is, however, so small that electronic effects do not greatly influence the basicities of these alcohols. Our result is hence in agreement with conclusions drawn from the anti-inductive basicity order of alcohols and ethers about the dominating effect of hydrogen bond formation and steric hindrance to solvation on the conversion of an alcohol to an oxonium ion.<sup>1,5</sup>

Attempts that were made to evaluate the basicity constant of diphenylmethanol by the same method were unsuccessful; this was possibly due to the Hammett-Chapman effect.<sup>7</sup>

1. Arnett, E. M. and Anderson, J. N. *J. Am. Chem. Soc.* **85** (1963) 1542.
2. Deno, N. and Wisotsky, M. J. *J. Am. Chem. Soc.* **85** (1963) 1735.
3. Virtanen, P. O. I. and Korpela, J. *Suomen Kemistilehti B* **41** (1968) 321.
4. Deno, N. C. and Turner, J. O. *J. Org. Chem.* **31** (1966) 1969.
5. Arnett, E. M., Wu, C. Y., Anderson, J. N. and Bushick, R. D. *J. Am. Chem. Soc.* **84** (1962) 1674.
6. Arnett, E. M. and Wu, C. Y. *J. Am. Chem. Soc.* **84** (1962) 1680.
7. Hammett, L. P. and Chapman, R. P. *J. Am. Chem. Soc.* **56** (1934) 1282.

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