THE PROTONATION OF SOME SATURATED ALCOHOLS IN AQUEOUS SULFURIC ACID[1,2]

Sir:

We wish to report measurements of the conversion to oxonium ion for several typical primary, secondary and tertiary aliphatic alcohols in aqueous sulfuric acid. Various attempts have been made previously to determine the pK_a's of simple alcohols in aqueous acid[3-7] and a review of this and allied problems will appear shortly.[8] Also, the need for such data has been pointed out in another recent article.[9] We have applied the solvent extraction–g.l.c. technique[10] to several closely related alcohols that represent the primary, secondary and tertiary series and whose solubilities and stabilities are suitable.

previous suggestion that steric hindrance to solvation is an important factor in the protonation of oxygen bases.[10]

The validity of the results given here is supported by their agreement with those obtained by Deno[8,13] for methanol using Raman spectroscopy and for several phenyl-substituted aliphatic alcohols using a different distribution method than that employed here. New support is given to the extraction–g.l.c. technique by the fact that our previous results[10] for THF have now been extended to cover five H_0 units through the use of the flame ionization detector. As before a 2% stock solution in cyclohexane was used. To our knowledge this is a greater range of acidity than has been used for any previous examination of the protonation of a weak base by any method. A logarithmic plot combining

TABLE I[a]

Alcohol	Strength of H_2SO_4 at Half-ionization, %	H_0^e	K'_D	Apparent slope of log plot	Column[f] temp., °C.	Flow rate, ml./min.	Concn. of alcohol stock sol., %
n-Butyl	39.5	−2.27	0.62	1.0	120	92	2[b]
		−2.39	0.44	0.96	120	92	2[b]
		−2.38	0.31	.70	115	35	0.02[c]
sec-Butyl	36.5	−2.16	0.23	.78	70	43	0.02[c]
t-Butyl[d]	41.5	−2.56	0.16	.78	85	66	2[b]
t-Amyl	38.5	−2.32	0.42	.67	70	41	0.02[c]

[a] The procedure was the same as that described in ref. 10 except that the volume of organic layer (isoöctane) was ten times that of the aqueous one. [b] Done with Burrell K-2 Kromotog using thermal conductivity cell. [c] Burrell K-D Kromotog used with flame ionization detector. [d] Could not be studied with flame ionization at lower concentration because of interfering solvent peak. [e] Paul and Long H_0 scale, *Chem. Rev.*, **57**, 1 (1957). [f] Six-foot Tween column with Helium eluent used throughout.

As a means of dealing with possible complications resulting from the association of these substrates in either or both phases of the distribution system, most of the experiments were repeated with widely varying concentrations of the alcohols so that if necessary an extrapolation to infinite dilution could be made. Employment of a flame ionization detector on the gas chromatograph[11] permitted us to go to much lower concentrations than had been possible previously. The only problem arising from this innovation was the appearance in one case of a large peak from solvent "tailing." Linear plots of log $D/(K_D − D)$ vs. H_0 (equivalent to spectrophotometric plots of log indicator ratio vs. H_0) were obtained in all cases over 2–3 H_0 units, and no evidence of decomposition was observed in the solutions employed. Constancy of the distribution ratio with changing alcohol concentration was established. The results listed in Table I show clearly that branching of the hydrocarbon chain has little effect on this measure of the basicities of these alcohols as is also the case for the corresponding amines.[12] In the present case the effect of changing structure on apparent basicity probably is too small to be resolved by the solvent extraction technique. Furthermore, their apparent basicities are quite appreciably greater than those of comparable ethers,[10] diethyl ether being half-ionized in 52% sulfuric acid and di-n-butyl ether in 68.1%. This result agrees with our

our old data[10] with the new was linear over the whole range but the slope which previously had been estimated as 0.92 now can be given with much more reliability as 0.66, the difference in slope arising from different weighting of terminal points.

Examination of what data are available from the literature[14] and from our laboratory suggests that most of the published values for slopes of log indicator ratio vs. H_0 for weak bases should be taken with considerable reserve and are seldom accurate to better than 0.1–0.2 slope unit. They usually are based on an acidity range of only 1.5 to 3 H_0 units with the upper and lower ends of the line in much greater doubt than that portion close to the half-ionization point. It seems likely that if such measurements could be extended accurately over a much wider range of acidity many slopes would be changed considerably. Weak bases with different slopes cannot in fact be referred to the same standard state and it is therefore improper to compare their basicities in terms of pK_a's.[16] Therefore we have used the H_0 at half-ionization to represent the operational measure of basicity-solvation changes. The alcohols reported here seem to have about the same slopes for their logarithmic plots and these are in the region of the new value cited for THF. It is possible that although the H_0 values at half-ionization do not correspond to the thermodynamic pK_a at the standard state for true Hammett indicators (whose slopes are 1.00) these oxygen bases may have an acidity function of their own. If this should be true, the H_0 values at half-ionization are a valid criterion of their basicities relative to each other. We currently are subjecting several other ethers to closer scrutiny over a wide acidity range to see if the slopes will be modified and also are measuring the protonation of other alcohols. In general it seems likely that compounds of similar structure will either have similar (but presently

(1) Stereoelectronic Effects in Organic Bases. X.

(2) Generously supported by Public Health Services Grant (A-3643 BBC).

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(11) A Burrell-KD instrument made available to us through the generosity of the Burrell Corporation.

(12) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79**, 5441 (1957).

(13) N. C. Deno, private communication. H_0 at half-ionization for methanol was found to be about −2.2.

(14) Many spectrophotometric studies of weak bases have employed the Davis-Geissman[15] treatment which gives no information at all about the slope of the indicator plot.

(15) C. T. Davis and T. A. Geissman, *J. Am. Chem. Soc.*, **76**, 3507 (1954).

(16) This failure of the Hammett activity coefficient postulate for exact treatment of many weak bases appears to be generally recognized now by most practitioners in this field.

unknown slopes) or slopes that vary with structure in some systematic way. If this is true it may be more proper to take the H_0 at half-ionization as a real measure of basicity within a series of related compounds than attempt to correct it for solvation by means of a slope which is not known with accuracy.

It will be noted that the H_0 at half-ionization does not change appreciably as the alcohol concentration is varied nor does it change as the slope of the plot is modified. So far in our experience there is no reason to question the published half-ionization points for most Hammett weak bases although as the slopes are better elucidated many thermodynamic pK_a's may be drastically altered. We suggest that some of the difficulties which have been found in kinetic interpretations of reactions involving alcohols are the result of their being very poor Hammett indicators (slopes widely different from unity) so that the fraction ionized does not vary with changing acidity in a way predicted by the H_0 function.

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THE CRYSTAL STRUCTURE AND MOLECULAR STRUCTURE OF DIBENZENECHROMIUM

Sir:

Fischer and Weiss[1] reported the correct unit cell for $Cr(C_6H_6)_2$ which *requires* that the molecule belong to the point group D_{3d} and *permits* it to belong to any group of higher symmetry having D_{3d} as a subgroup. However, they and Ruch[2] proposed a theory of bonding which led them to postulate that the molecule *should* have only a threefold and not a sixfold axis. Evidence from vibrational spectra both for,[3] against[4] and again for[5] threefold symmetry has been reported.

In the meantime, in 1960, Jellinek[6] had reported that using X-ray diffraction intensities for 177 reflections (not further specified) a set of atom positions had been determined, giving for the usual reliability index the impressive value of 6.3%. No details of the data collection or the distribution of data over the reciprocal lattice and very few concerning the refinement were mentioned. The carbon atom positions corresponded to D_{3d} symmetry with planar rings having alternating bond distances of 1.439 and 1.353 Å. with standard deviations of only 0.014 Å.

Ordinarily, a structure would have been considered firmly established under these circumstances, but in this case doubts remained. This was at least partly because a satisfactory molecular orbital treatment of the bonding can be constructed[7] without reduction of the sixfold symmetry of the rings, although distortion of the type invoked by Fischer would not necessarily have any pronounced effect on the bonding and at least one qualitative suggestion of a cause for such distortion has been put forward.[8] A more recent investigation,[9] however, led to the conclusion that there is no

apparent way to account for distortion to D_{3d} symmetry.

Thus, the position is that theoretically, distortion seems unnecessary and not easily explained, while experimentally there has been reported one seemingly reliable evidence for it, although there does not appear to be any other evidence which is decisive either way. It thus appeared that the evidence for low symmetry deserved re-examination and an independent re-investigation of the crystal structure was therefore undertaken. This note is a preliminary report of the results.

Three dimensional data were gathered by usual techniques, but with considerable care, at room temperature, using a Weissenberg camera and $MoK\alpha$ radiation.[10] Levels $hk0$–$hk9$ were recorded on equi-inclination photographs. A total of 270 independent reflections of measurable intensity were recorded and their intensities estimated visually. On upper layers, only the extended spots were used and they were corrected for elongation.[11] Because of the general occurrence of equivalent reflections (hkl, klh, lhk) in the cubic space group, random errors in the photographic records are unlikely to have escaped detection. After Lp corrections, the data were placed on a common scale by intercomparison of films, and approximate absolute scaling and temperature factors were obtained by Wilson's method.[12] Since chromium atoms do not contribute to reflections with mixed indices, separate temperature factors and scale factors for Cr and C atoms were obtained using two Wilson plots. The scale factors were quite close.

A set of trial carbon positions was obtained and a few cycles of least squares refinement were carried out in which the carbon positions, an over-all scale factor and isotropic temperature factors were varied. A residual, $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, of 0.104 was obtained. The next step, an extremely important one, was concerned with eliminating the effects of spurious discrepancies in scale factors from one set of films to another. In this particular case, the difficulty arises because reflections on the hkl (l even) films can only be placed on the same scale as those from the hkl (l odd) films by comparing different records of spots with mixed indices. These are produced only by the carbon and hydrogen atoms and are thus in general relatively weak. In order to minimize the effect of interfilm scaling errors from this source, the refinement program was modified to permit separate scale factor adjustment for the two classes of data. Three more cycles of full matrix refinement were now carried out, giving the following results (standard deviations in parentheses): C–C 1.386 (0.017) and 1.407 (0.017); Cr–C: 3.132 (0.012), 2.138 (0.012); Cr–center of mean plane of C's: 1.616 (0.010); deviation of each carbon atom from mean plane: 0.004; $R = 0.061$ based on observed reflections, with no unobserved reflection giving $F_c > |F_{min}|$ where $|F_{min}|$ is for the weakest observed reflection; R over all reflections in the range of observation: 0.115.

In view of the fact that the contribution of the hydrogen atoms is not entirely negligible compared to that of the carbon atoms, it was considered important to check their influence upon the above carbon atom positions. A three-dimensional difference Fourier map was there-

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