Protonation of Alcohols by Hydrogen Bromide in Dibromodifluoromethane; Rates of Proton Exchange and Alcohol Basicity

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Alcohols are protonated by HBr in CBr_2F_2, and at low temperatures separate ^1H n.m.r. signals for HBr and ROH_2^+ are observed. Line-shape analysis of the n.m.r. spectra at different temperatures has been used to determine the rates of proton exchange between HBr and the protonated alcohol. The rates are well correlated with the Taft σ_I parameter for the alcohols and provide an order of basicities for these weak bases in CBr_2F_2.

Strong acids such as HBF_4,[1] H_2SO_4,[2] and HSO_3F[3] are capable of protonating alcohols. The strongest acid system, HSO_3F–SbF_5, has been particularly well studied[4–6] since these solutions, diluted with SO_2 or SO_2ClF, give clearly resolved spectra at low temperatures with all the features and fine structure expected for protonated alcohols. At room temperatures and above, decomposition of the alcohols occurs and methanol in HSO_3F–SbF_5 shows spectral changes at 260 K which indicate chemical reaction to be occurring.[7] At lower temperatures, alcohols in HSO_3F–SbF_5 appear to be fully protonated and no evidence for labile proton exchange between acid and ROH_2^+ has been found.

Despite the drawbacks to using these superacids in studying the protonation of alcohols, the use of other acids has been neglected, presumably because they were invariably weaker. However we have been able to show that HBr in CBr_2F_2 is capable of protonating ketones and aldehydes,[8] and in a brief communication it was reported that H_3O^+ and $CH_3OH_2^+$ were formed in this acid medium.[9]

We now report more fully on the behaviour of alcohols: nine primary, four secondary, and a tertiary alcohol have been studied. The system HBr–CBr_2F_2 reveals itself to be an excellent medium for the study of the protonation of alcohols, being relatively free from side reactions and permitting the study of the kinetics of proton exchange.

Experimental

Hydrogen bromide was purified by repeated passage through a trap cooled at 195 K (CO_2–Me_2CO) which removed H_2O and Br_2. CBr_2F_2 was purified by vacuum-line distillation. Solutions were prepared by addition of a measured volume or weight of the alcohol to a solution of HBr in CBr_2F_2 (generally 0.010 cm^3 in 0.500 cm^3). CD_2Cl_2 was added as internal lock and $SiMe_4$ as internal reference.

The ^1H n.m.r. spectra were recorded with a Bruker HFX 90 MHz Fourier transform spectrometer equipped with a variable-temperature unit. Line-shape analysis was carried out with the program LSHAPE,[10] details of which have been reported.[8]

For the proton-exchange reactions (1) the exchange rates

$$ROH + HBr \underset{k(ROH_2^+,\,Br^-)}{\overset{k(HBr,\,ROH)}{\rightleftharpoons}} ROH_2^+ + Br^- \qquad (1)$$

may be determined by measuring the line-broadening of the acid (HBr) and conjugate acid (ROH_2^+) signals, provided these are clearly differentiated in the n.m.r. spectrum.[8] The exchange rates (k_A for the acid site, k_B for the base) are directly related to ΔW_A and ΔW_B, for broadenings of the signals as compared with the line-width in the absence of exchange. The overall rate constant k is the average of these, *i.e.* $(k_A + k_B)/2$.

The second-order rate constants for the proton-transfer processes of (1) are related by the equations (2) and (3).

$$k(HBr, ROH) = k_A/[ROH] \qquad (2)$$

$$k(ROH_2^+, Br^-) = k_B/[Br^-] \qquad (3)$$

However under our reaction conditions, with HBr in excess over ROH, reaction (1) in the forward direction is essentially complete and [ROH] is immeasurably low. By the same token the equilibrium concentration of Br^- is the same as the original concentration of ROH. Hence only $k(ROH_2^+, Br^-)$ can be evaluated and values are reported in Table 1 for the fourteen alcohols at a common temperature of 163 K.

Discussion

HBr is strong enough to protonate alcohols and phenols in CBr_2F_2 solution. This solvent has some advantages for ^1H n.m.r. studies since it has the twin merits of low freezing point (132 K) and low chemical reactivity. Moreover it offers no site for protonation and its oxidising capability is insignificant. In these respects HBr–CBr_2F_2 is superior to the sulphuric and sulphonic acid systems enhanced by strong Lewis acids such as SbF_5. However, HBr–CBr_2F_2 does have the disadvantages of weaker acidity and conjugate base reactivity; Br^- is likely to be a strong nucleophile in this solvent. This drawback was turned to advantage in studying CH_3CHO in this system, when the hitherto unknown 1-bromoethanol was found to be present and to be stable at low temperatures.[8]

A further complication in HBr–CBr_2F_2 arises because proton exchange between the protonated alcohol and HBr takes place readily. This means that the n.m.r. signals are less well resolved than those of ROH_2^+ in HSO_3F–SbF_5 diluted with SO_2 or SO_2ClF. Nevertheless HBr–CBr_2F_2 offers the advantage that the kinetics of proton exchange can be studied.

In our previous paper[8] we reported on a variety of ketones and some aldehydes that were protonated by HBr–CBr_2F_2. Separate signals for R_2COH^+ and HBr were distinguishable at low temperatures, showing that proton exchange was slow on the n.m.r. timescale. From the line-shape analysis of these signals $\log[k(R_2COH^+, Br^-)]$ was obtained but no relationship with reported pK_{BH^+} values for ketones could be established.[9]

In turning to alcohols, we were aware that pK_{BH^+} values are sparse and only a few are reported for the simpler molecules.[11] Early spectrophotometric measurements for solutions of alcohols in acetic acid containing $HClO_4$ and an indicator had revealed the order of decreasing basicities $H_2O > Pr^iOH >$

Table 1. Rate data for protonation of alcohols and phenols at 163 K

	[ROH]/M	[HBr]/M	$\log(k_B/s^{-1})$	$\log[k(ROH_2^+, Br^-)/dm^3 mol^{-1} s^{-1}]$	$\sigma_I(R)$[a]
Primary alcohols					
CH_3OH	0.286	1.001	2.95	3.50	−0.046
CH_3CH_2OH	0.199	0.837	2.41	3.11	−0.055
$CH_3[CH_2]_2OH$	0.150	2.418	2.25	3.07	−0.057
$CH_3[CH_2]_3OH$	0.127	0.837	2.18	3.07	−0.058
$CH_3[CH_2]_4OH$	0.108	0.837	2.09	3.05	−0.061
$CH_3[CH_2]_5OH$	0.0928	0.837	2.19	3.23	−0.061
$(CH_3)_3CCH_2OH$	0.0847	0.847	2.00	3.07	−0.062
$C_6H_5CH_2OH$	0.113	0.837	3.08	4.03	−0.026
$CH_2{=}CHCH_2OH$	0.172	0.837	2.94	3.70	N.a.
Secondary alcohols					
$(CH_3)_2CHOH$	0.152	0.837	1.87	2.69	−0.064
$CH_3CH_2CH(CH_3)OH$	0.189	0.833	2.05	2.78	−0.066
$CH_3[CH_2]_2CH(CH_3)OH$	0.108	0.423	1.93	2.91	N.a.
$(CH_3)_3CCH(CH_3)OH$	0.0926	0.837	1.43	2.46	−0.072
Tertiary alcohol					
$(CH_3)_3COH$	0.0829	0.840	0.75	1.83	−0.074

[a] Values taken from Tables I and IA of ref. 13*b*; N.a. = not available.

Table 2. ^1H N.m.r. data for exchange-proton signals of alcohols and phenols in $HBr{-}CBr_2F_2$ at low temperatures[a]

	T/K	$\delta(ROH_2^+)$	Line-width of ROH_2^+ signal (Hz)	δ(HBr)	Line-width of HBr signal (Hz)
Primary alcohols					
CH_3OH (1:3.5)[b]	163	12.12	356	−2.28	126.6
	148	12.12	100	−2.33	35.0
CH_3CH_2OH (1:4.2)	168	12.06	190.3	−2.19	85.2
	143	12.03	29.8	−1.98	8.8
$CH_3[CH_2]_2OH$ (1:16)	173	12.08	209.8	−2.40	66.6
	143	11.99	37.1	−2.20	14.7
$CH_3[CH_2]_3OH$ (1:6.6)	173	11.53	313.3	−2.20	170.0
	158	12.09	69.9	−2.17	33.3
$CH_3[CH_2]_4OH$ (1:7.8)	173	11.93	225.3	−2.58	91.6
	143	12.02	36.7	−2.28	6.6
$CH_3[CH_2]_5OH$ (1:9.0)	173	11.66	176.6	−2.47	57.1
	148	11.90	37.3	−2.33	8.7
$(CH_3)_3CCH_2OH$ (1:10)	183	11.94	809.4	−2.58	76.6
	143	12.03	24.9	−2.35	13.3
$C_6H_5CH_2OH$ (1:7.4)	158	11.55	345.0	−2.15	141.7
	138	12.00	221.0	−2.13	25.1
$CH_2{=}CHCH_2OH$ (1:4.9)	163	11.52	407.1	−1.99	272.9
	138	12.07	140.6	−2.01	13.2
Secondary alcohols					
$(CH_3)_2CHOH$ (1:5.5)	178	12.42	196.3	−2.32	79.4
	143	11.83	17.3	−2.05	5.2
$CH_3CH_2CH(CH_3)OH$ (1:4.4)	183	11.85	280.5	−2.50	56.7
	147	11.80	10.0	−2.23	5.6
$CH_3[CH_2]_2CH(CH_3)OH$ (1:3.9)	178	12.01	172.7	−2.13	108.4
	153	11.86	29.6	−1.80	15.9
$(CH_3)_3CCH(CH_3)OH$ (1:9.0)	183	12.06	226.6	−2.19	106.5
	158	11.87	26.6	−2.12	13.3
Tertiary alcohol					
$(CH_3)_3COH$ (1:10)	183	12.06	92.3	−2.44	42.6
	158	11.84	11.9	−2.20	8.9

[a] For each alcohol the higher temperature is that at which ROH_2^+ is first recognized as a separate signal; the lower is the temperature at which the spectrum showed the sharpest signals. [b] Molar ratio ROH:HBr.

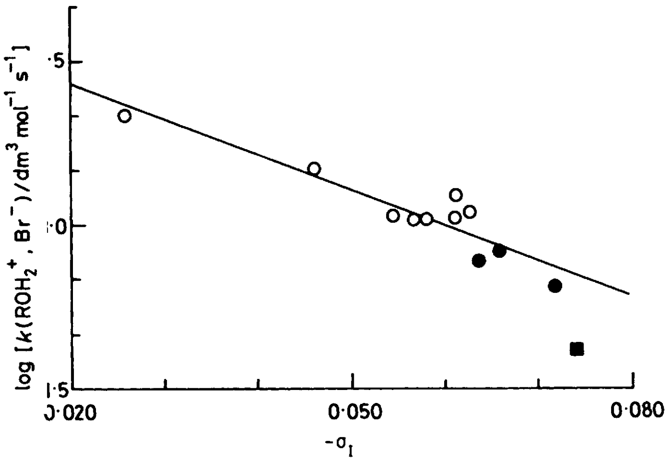

Figure. Plot of log$k$(ROH$_2^+$, Br$^-$) against the Taft parameter σ_I (○ = primary, ● = secondary, ■ = tertiary alcohols)

EtOH > MeOH.[12] A similar order was proposed on the basis of the relative solubility of HCl in alcohols.[13]

The proton resonance of HBr solutions in CBr_2F_2 is found to be *upfield* of the reference signal, again this being an advantage for line-shape analysis since it is well away from the rest of the spectrum. The signal varies with temperature however, *e.g.* δ −3.26 at 308 K, −3.11 at 173 K, and −2.80 at 148 K. As Table 2 shows, this signal remains upfield in all the systems reported here.

On adding the alcohol to HBr–CBr_2F_2, with the acid in excess, a single signal for the labile proton is observed at room temperature. On cooling this becomes broader until at 183 K it is extremely broad. Below this temperature it is resolved in two broad peaks, one downfield at *ca.* 12, attributable to the protonated alcohol, and the other upfield due to the HBr. These peaks sharpen rapidly on further cooling down to 138 K, the limit of our observations. At this temperature, proton exchange remains sufficiently rapid that relatively broad signals are observed for the protons of HBr and ROH_2^+ and this obscures any fine structure. The increased viscosity at the very low temperatures may also be partly responsible for signal breadth.

For t-butyl alcohol there was evidence of some chemical reaction but no detailed investigation was carried out. For this reason the data in Tables 1 and 2 for this alcohol are less precise than the results for other alcohols. In Table 2 the data for the ^1H n.m.r. signals of ROH_2^+ and HBr are given at the highest temperature at which they could be resolved and at the lowest temperature at which the signals were the sharpest.

The values of log$k$(ROH$_2^+$, Br$^-$) deduced by the line-shape analysis are given in Table 1. These rate coefficients refer to the reaction of the protonated alcohol with bromide ion, presumably within an ion pair, to give back the alcohol and HBr. Signals in the n.m.r. spectrum corresponding to the unprotonated ROH were not detected, so that the reported rate coefficients are for a strongly thermodynamically unfavourable reaction.

In the Figure, log$k$(ROH$_2^+$, Br$^-$) is plotted against the Taft parameters σ_I.[13] The equation of the straight line though the experimental points obtained by unweighted linear regression analysis is given in equation (4).

$$\log k(\mathrm{ROH_2^+, Br^-}) = +32.3\,\sigma_I + 4.94 \qquad (4)$$

The strongly thermodynamically favoured protonation of ROH by HBr may occur at the diffusion-limited rate. If this is the case then the value of log$k$(ROH$_2^+$, Br$^-$) along the series of alcohols will vary inversely with the equilibrium constant for protonation of the alcohol. It therefore follows that k(ROH$_2^+$, Br$^-$) will vary inversely with the basicity of the alcohol. The order of increasing basicities for ROH deduced in this way is that expected from increasing electron release by R and its consequent stabilisation of ROH_2^+. Thus the alcohols $CH_3[CH_2]_nOH$ become stronger bases as n increases. Secondary alcohols are more basic than primary alcohols, and t-butyl alcohol, the only tertiary alcohol investigated, is the most basic of all. It is almost two pK units more basic than CH_3OH. The primary alcohols benzyl and allyl alcohols are the least basic of all.

Our studies on other weak bases in the system HBr–CBr_2F_2 are continuing.

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