Solutions of Carbonyl Compounds in Dibromodifluoromethane in the Presence of Hydrogen Bromide: Protonation of Ketones and Formation of 1-Bromo-alcohols from Aldehydes

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HBr in CBr_2F_2 is capable of protonating a variety of ketones, and at low temperatures separate ^1H n.m.r. signals can be seen for the acid and protonated base. Line shape analysis of the signals enables rates of protonation to be calculated. Aldehydes in HBr–CBr_2F_2 give n.m.r. spectra that are consistent with the formation of 1-bromo-alcohols.

SOLUTIONS of hydrogen bromide in dibromodifluoromethane are a strongly acidic solvent system capable of converting alcohols into their conjugate acids.[1] Although not as powerfully acidic as fluorosulphuric acid or trifluoromethanesulphonic acid, the system has certain advantages for the n.m.r. study of protonated organic bases. Because of the low freezing point of CBr_2F_2 (132 K), it is suitable for work at low temperatures at which proton transfers between the solvent acid and the conjugate acid of a dissolved base are slowed down sufficiently to allow the detection of their separate proton signals.[1] However, viscosity broadening at very low temperatures imposes a limitation on the range of feasible measurements.

There are two important differences between the chemical characteristics of HBr in CBr_2F_2 and acidic systems containing sulphonic acids or Lewis acids, such as antimony pentafluoride. The former system has the advantage of having a very low oxidising capability so that side reactions involving electron or oxygen transfer have not so far been detected. On the other hand, the conjugate base formed, the bromide ion, has a high nucleophilicity and Lewis basicity in the aprotic solvent CBr_2F_2 whereas the conjugate bases of the so-called superacids are weak nucleophiles.

The present paper reports n.m.r. studies of aldehydes and ketones which illustrate these properties.

EXPERIMENTAL

Hydrogen bromide was purified by repeated passage of the gas through a trap cooled at 195 K (CO_2–acetone) which removed water and bromine. CBr_2F_2 was purified by vacuum-line distillation. Carbonyl compounds were distilled before use. Solutions were prepared by addition of a measured volume or weight of the carbonyl compound to a solution (0.5 cm^3) of HBr in CBr_2F_2 (usually 0.685M, *i.e.* 0.010 cm^3 HBr in 0.500 cm^3 CBr_2F_2). Deuteriated dichloromethane was added as internal lock and tetramethylsilane as internal reference.

The ^1H n.m.r. spectra were recorded on a Bruker HFX (90 MHz) Fourier transform spectrometer equipped with a variable-temperature unit. The appearance of the spectra and their interpretation is given in the Discussion section. To study dynamic effects, line-shape analysis was carried out using the program LSHAPE,[2] based on a method devised by Moore,[3] itself a refinement of the analysis given by Gutowsky and Holm,[4] and McConnell.[5] LSHAPE allows the optimization of the residence times, linewidths in the absence of exchange, chemical shifts, and fractional populations (if not otherwise known) of the two sites of protonation so as to obtain the best fit of the data to the line-shape equations.

For a simple proton exchange between two environments (HBr and HB^+, where HB^+ represents the protonated organic solute base B) proceeding *via* the proton-transfer reactions (1) the exchange-induced line broadening of each of the signals for two sites is, in the slow-exchange situation, when the individual signals do not overlap, simply related to the mean residence times (τ) of the protons in the two environments. (The reciprocal of a mean residence time is itself the pseudo-first-order rate coefficient for the chemical flux [6] out of the chemical species concerned.) Equations (2) set out the basic relationships where W_{HX} and W_{HX}° are the line widths of the signals due to HX in the presence and absence of exchange under the same conditions, respectively.

$$\mathrm{HBr} + \mathrm{B} \underset{k_{\mathrm{HB,Br}}}{\overset{k_{\mathrm{HBr,B}}}{\rightleftharpoons}} \mathrm{Br}^- + \mathrm{HB}^+ \qquad (1)$$

$$\left.\begin{aligned} k_a &= \tau_{\mathrm{HBr}}^{-1} = \pi(W_{\mathrm{HBr}} - W_{\mathrm{HBr}}^\circ) \\ k_b &= \tau_{\mathrm{HB}}^{-1} = \pi(W_{\mathrm{HB}} - W_{\mathrm{HB}}^\circ) \end{aligned}\right\} \qquad (2)$$

An overall rate constant k is related to k_a and k_b [equations (3) and (4)]. The second-order rate constants for the fundamental proton-transfer processes of equation (1) can be derived from the observed first-order rate coefficients k_a and k_b by dividing by the concentration of the base (proton acceptor) concerned, *i.e.* equations (5) and (6).

$$k = (k_a + k_b)/2 \qquad (3)$$

$$\left.\begin{aligned} k_a &= 2p_{\mathrm{HB}}k \\ k_b &= 2p_{\mathrm{HBr}}k \end{aligned}\right\} \qquad (4)$$

$$k_{\mathrm{HBr,B}} = k_a/[\mathrm{B}] \qquad (5)$$

$$k_{\mathrm{HB,Br}} = k_b/[\mathrm{Br}^-] \qquad (6)$$

In our system, the stoicheiometric concentration of hydrogen bromide always exceeded that of the organic base, and, since the reaction (1) is essentially complete in the forward direction, the relevant equilibrium concentration of bromide ion is virtually equal to the stoicheiometric concentration of added base.

On this basis equation (6) was used for the evaluation of $k_{\mathrm{HB,Br}}$. The calculation of $k_{\mathrm{HBr,B}}$ is not possible by the corresponding procedure because the (very low) concentration

TABLE 1

Rate data for protonation of ketones at a temperature of 183 K

Ketone	$[HBr]_{stoic}$/M	[Ketone]/M	$\lg(k_b/s^{-1})$	$\lg(k_{HB,Br}$/ l $mol^{-1} s^{-1})$	pK_{BH^+}
2,6-Dimethyl-4-pyrone	0.454	0.061	1.69	2.9	+0.3 [a]
Pentan-3-one	0.504	0.100	2.3	3.3	−2.9 [b]
2,2,4,4-Tetramethylpentan-3-one	0.542	0.061	2.49	3.7	−3.5 [b]
Butan-2-one	0.496	0.118	2.86	3.8	−7.2 [c]
3,3-Dimethylbutan-2-one	1.19	0.069	3.0	4.2	−7.1 [c]
Cyclohexanone	0.502	0.102	3.17	4.2	−3.1,[b] −6.8 [c]
Cyclopentanone	0.526	0.080	3.43	4.5	−2.3,[b] −7.5 [c]
3,5,5-Trimethylcyclohex-2-enone	0.483	0.117	4.03	5.0	−2.8 [d]

[a] G. C. Levy, J. D. Cargioli, and W. Racela, *J. Am. Chem. Soc.*, 1970, **92**, 6238. [b] A. R. Butler, *J. Chem. Soc., Perkin Trans. 2*, 1976, 959. [c] Ref. 16. [d] R. I. Zalewski and G. E. Dunn, *Can. J. Chem.*, 1969, **47**, 2263.

of residual unprotonated base B in the system is not similarly accessible. Values of $\lg(k_{HB,Br})$, interpolated or extrapolated to a common temperature of 183 K, are listed in Table 1.

DISCUSSION

Butan-2-one, in a molar ratio of 1 : 5 with HBr (0.5M) in CBr_2F_2 at 293 K shows the expected sharp signals for the protons on carbons but a broad signal (10 Hz) for the proton of HBr at δ −2.17. As the temperature is lowered, this signal moves downfield to δ −0.04 at 243 K and +0.83 at 203 K. At this latter temperature the signal is *ca.* 100 Hz wide and underlies the CH_3 triplet of the ethyl group.

TABLE 2

^1H N.m.r. data for exchange-proton signals of ketones in $HBr–CBr_2F_2$ at low temperatures [a]

Ketone (ketone : HBr) [b]	T/K	δ(HBr)	Line-width HBr signal (Hz)	$\delta(COH^+)$	Line-width COH^+ signal (Hz)
2,6-Dimethyl-4-pyrone	203	−1.97	22.3	12.70	105
(1 : 8.5)	183	−1.80	9.9	12.47	25.9
Pentan-3-one	183	1.82	79.9	13.51	119.2
(1 : 6)	158	3.04	42.7	13.15	66.9
Butan-2-one	178	5.31	116.7	13.40	163.3
(1 : 5.1)	163	5.32	19.7	13.20	54.0
2,2,4,4-Tetramethylpentan-3-one	193	−2.01	53.3	13.30	266.0
(1 : 9.8)	153	−0.65	38.3	13.90	56.6
3,3-Dimethylbutan-2-one	183	0.95	150.0	12.96	400
(1 : 17.2)	148	0.94	18.1	13.03	40.9
Cyclohexanone	168	2.96	124.0	13.33	152
(1 : 5.9)	143	4.35	20.0	12.55	23.5
Cyclopentanone	178	−0.14	53.3	13.34	537
(1 : 7.6)	153	0.40	8.9	12.93	86.3
3,5,5-Trimethylcyclohex-2-enone	163	−0.64	50.0	15.20	187
(1 : 5.1)	138	−0.48	12.1	14.78	18.5

[a] For each ketone the higher temperature is that at which the COH^+ was first recognised as a separate signal, the lower is the lowest temperature at which a spectrum was recorded. [b] Mole ratio.

At 183 K its width is 175 Hz and the CH signals are viscosity-broadened, losing their fine structure altogether at 173 K. Below this temperature the HBr signal begins to sharpen and move upfield again to δ −0.03 (140 Hz) at 168 K and −0.33 (95 Hz) at 163 K. At this temperature a downfield signal at δ *ca.* 13 is just discernible. This becomes more prominent as the temperature is further lowered. It is in the expected region for protonated ketones [7-9] and is ascribed to the OH^+ of $CH_3CH_2C(OH^+)CH_3$. Similar observations for other ketones are listed in Table 2. The highest temperatures at which separate signals were observed (at the particular concentrations examined) were: 2,6-dimethyl-4-pyrone, 203 K; 3,5,5-trimethylcyclohex-2-enone, 173 K; pentan-3-one, 3,3-dimethylbutan-2-one, and cyclopentanone, 183 K; and cyclohexanone, 168 K. These are much lower than those required to resolve the peaks in magic acid.[10] The chemical shifts of the protonated ketones are *ca.* 0.7 p.p.m. upfield from their position in the superacids. Table 2 lists the chemical shifts and linewidths of the HBr and OH^+ signals at the highest and lowest temperatures at which separate signals were observed.

Splitting of the OH^+ signal due to *E*- and *Z*-isomers was not observed for the aliphatic ketones, whereas in the superacids this can be clearly seen.[9,11] However at these low temperatures proton residence times on the carbonyl oxygen and bromine atoms are sufficiently long to permit of observation by ^1H n.m.r. spectroscopy and are amenable to line-shape analysis.

The values of $k_{HB,Br}$ (Table 1) reflect the ease with which the protonated ketones give up a proton to the bromide ion. The values of this 'kinetic acidity' of the organic cations relative to the bromide ion as a reference base are expected to follow the same sequence as the pK_{HB^+} values for the corresponding compounds. In similar studies with fluorosulphuric acid–antimony pentafluoride as the acidic solvent system we have shown that the rate of protonation of the base by the acidic solvent is an encounter-controlled process and accordingly have concluded that the rate constants for the reverse process, proton loss (in that solvent system), are proportional to the $K_{\mathrm{HB^+}}$ values.* In the absence of similar information about the rates of protonation of the bases we cannot go so far to assert that the $k_{\mathrm{HB,Br}}$ values in the present paper are proportional to the $K_{\mathrm{HB^+}}$ values, but they might be expected to follow the same trend, if a Brønsted relation between rate and equilibrium constants is valid.

Dibromodifluoromethane is a solvent of low relative permittivity, <3 (dielectric constant), and the pair of ions which is the reaction product in equation (1) is expected to be predominantly associated into ion pairs. However, this should not complicate the kinetic analysis. It implies only that the backward reaction of (1) is a proton transfer within an ion pair.

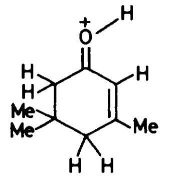
The sequence of rate constants 3,5,5-trimethylcyclohex-2-enone (I) $>$ cycloalkanones $>$ alkanones $>$ 2,6-dimethyl-4-pyrone (II) cannot necessarily be accepted as the order of the basicities of the ketones as Table 1 shows. The uncertainty over $pK_{\mathrm{BH^+}}$ values for the ketones makes comparison difficult. The two strongest bases, the αβ-unsaturated ketones, show the lowest and highest rate constants for proton transfer from the protonated ketone to bromide ion in the series of ketones studied, and this observation is not consistent with any simple relationship.

The finding that the temperatures at which discrete signals for the two protons sites between which exchange occurs in dibromodifluoromethane–hydrogen bromide is much lower than for the same bases in fluorosulphuric acid solution immediately indicates that the former solvent system is considerably less acidic than superacids. This is consistent with the observation that 2,6-dimethyl-4-pyrone is monoprotonated in our solutions whereas it is diprotonated in ' magic acid '.[12]

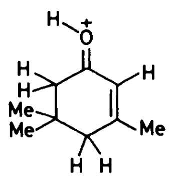
Of the ketones studied in HBr–CBr_2F_2 only protonated (I) and (II) showed direct evidence of *E*,*Z*-isomerism. With these cyclic ketones the signals of the olefinic protons adjacent to the protonated carbonyl group were split. In the case of (I) signals at δ 7.30 and 6.83 (at 153 K) were observed for the olefinic CH corresponding to the two structures (Ia and b).

When 2,6-dimethyl-4-pyrone is dissolved in HBr–CBr_2F_2 it is singly protonated and below 203 K the separate signal for the proton attached to the carbonyl oxygen is at δ 12.7, whereas in the more acidic HSO_3F–SbF_5 double protonation of the carbonyl oxygen is observed.[12] The ^1H n.m.r. spectrum of (II) shows that rotation about the C–OH bond is relatively slow, *i.e.* the carbonyl bond retains some of its double-bond character upon single protonation in HBr–CBr_2F_2. Separate signals at δ 7.39 and 7.92 are seen for the CH protons at the 3- and 5-positions, at 213 K. On cooling to 173 K they form an irregular quartet due to coupling between themselves. That this splitting pattern was not due to coupling with the methyl protons was shown by decoupling of the methyl protons which left the 3- and 5-proton signals unaffected.

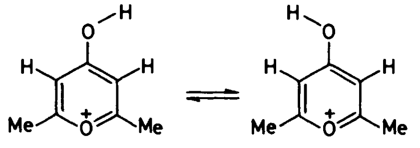
Aldehydes.—The protonation of aldehydes by very strong acids has been observed on several occasions. Olah has reported the effects of HSO_3F–SbF_5–SO_3 on six aldehydes,[13] Hogeveen used HF–BF_3 on five aldehydes,[14] and Brouwer used HF–SbF_5 on acetaldehyde.[8] In all cases the protonated aldehyde was identified by the appearance of signals due to the OH^+ which appeared at δ *ca.* 14—17. These signals were complex. This is due partly to coupling with the CH aldehyde protons (observed in the expected δ 4—10 region) and partly to their being *E*- and *Z*-isomers. In the case of CH_3CHOH^+ the ratio of *E* : *Z* was 4 : 1.[10] There was no evidence of aldehyde condensation occurring in these strong acid solutions, nor was this observed in HBr–CBr_2F_2. However a reaction between the aldehyde and the acid does take place.



(Ia)



(Ib)



(II)

Since Br^- should be a strong nucleophile in CBr_2F_2, HBr should react with an aldehyde as in (7). The

$$RCHO + HBr \longrightarrow RCH(OH)Br \qquad (7)$$

product of such a reaction, a 1-bromoalcohol, has never been isolated nor reliably reported, nor indeed is expected to be stable since dehydrobromination should occur to form the aldehyde. It appears, however, that the 1-bromoalcohol is stable at the low temperatures attainable in CBr_2F_2. Our evidence for the formation of 1-bromoalcohols rests solely on ^1H n.m.r. spectroscopy and principally on the CH signal which shifts from the δ 9—10 region of an aldehyde to *ca.* 6 p.p.m. Such an upfield shift of 3.5 p.p.m. can only mean a complete bonding and substituent change in its immediate vicinity. In protonated aldehydes the CH signal is *ca.* 10 p.p.m.[13,14] Studies on the hydrated forms of aldehydes, $RCH(OH)_2$, show upfield changes of *ca.* 5 p.p.m. for this CH proton.[15]

When acetaldehyde is added to HBr–CBr_2F_2 at 213 K the ^1H n.m.r. spectrum shows signals at δ 2.01 (3 H, d) due to CH_3 and at δ 6.10 (1 H, q) due to CH. We interpret this as being due to coupling of the CH and CH_3 groups of $CH_3CH(OH)Br$ with one another but not with

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* See footnotes to Table 1.

the OH proton; the same is observed in ethanol itself when a trace of acid is present. Rapid proton exchange between the OH and HBr results in a merged signal which in this case is at δ −3.00.

The spectrum of 2-methylpropanal in $HBr-CBr_2F_2$ was likewise consistent with its being converted into 1-bromo-2-methylpropanol, $(CH_3)_2CHCH(OH)Br$: δ 1.08 (6 H, d) due to the two CH_3 groups (shifted from δ 1.12 in the aldehyde); δ 2.15 (1 H, m) due to the methine proton (shifted from δ 2.38); and δ 5.98 (1 H, d) due to the proton on the alcohol carbon (shifted from δ 9.58 in the aldehyde). Again the OH signal was not observed but below 163 K there was the appearance of a very broad signal at δ *ca.* 12.5 which could represent the OH_2^+ protons.

2,2-Dimethylpropanal also showed a signal, at δ 6.59, for the CH proton of $(CH_3)_3CCH(OH)Br$, when dissolved in $HBr-CBr_2F_2$. Cooling this solution to 153 K did not give rise to a distinct OH signal.

By analogy with the reduced extent of hydration of the carbonyl group in ketones, compared to aldehydes, attack of Br^- on ketones to form $R^1R^2C(OH)Br$ is expected to be less important. The least hindered of the ketones is acetone and is therefore possibly the one most likely to react with HBr in this manner. Indeed acetone solutions in $HBr-CBr_2F_2$ did behave differently from the other ketones. The main feature was the appearance in the ^1H n.m.r. spectrum of a sharp signal at δ 2.91. This may arise from the methyl protons of $(CH_3)_2C(OH)Br$. However most of the acetone was not involved in this reaction as shown by the main CH_3 signal in the spectrum. Moreover, the behaviour of these solutions was uncharacteristic in that the changes were not temperature-reversible. Further investigations into acetone–$HBr-CBr_2F_2$ will be needed to clarify its behaviour.

Acetone in $HBr-CBr_2F_2$ at 253 K shows only CH_3 (at δ 2.39) and HBr signals (at δ −1.33). Cooling to 233 K broadens the latter and splits the former into an uneven doublet (δ 2.77 and 2.91) but does not show a signal for COH^+. As the temperature is further lowered the signals become broader but even at 144 K, when the doublet structure of the methyl signal is lost, there is still no signal for COH^+. The unevenness of the methyl ' doublet ' (ratio δ 2.77 : δ 2.91 is 3 : 1) means that it cannot arise from *E*- and *Z*-isomers as observed for acetone in $HSO_3F-SbF_5-SO_3$ and where the coupling to the COH^+ proton (observed at δ 14.93) produced complex multiplets for the methyl signals.[9] Nor is the COH^+ signal normally hard to observe for acetone.[7]

That the signal of δ 2.91 was not due to 2-bromopropan-2-ol $CH_3C(OH)BrCH_3$ was indicated by the absence of signals other than those of acetone in the ^{13}C n.m.r. spectrum. This showed δ 31.38 (CH_3), shifted from 28.98 p.p.m. in neat acetone, and δ 233.09 (CO), shifted from 204.65 p.p.m.

Clearly, acetone in $HBr-CBr_2F_2$ is a special case. The ^{13}C n.m.r. spectrum shows that some interaction has occurred and the ^1H n.m.r. spectrum shows the elusive proton at δ 2.91. The absence of a COH^+ signal shows that either exchange of this group with HBr is too rapid to be observed, even at 144 K, or that there is another protonated acetone species present in which the proton resonance is upfield at δ 2.91. One possible explanation is the formation of a strongly hydrogen-bonded complex, say $(CH_3)_2CO-HBr$, which is unexpectedly stable in the medium. The difference in behaviour between acetone and other ketones is a well known phenomenon partly due to its basicity [16] and partly due to steric factors.

The HBr Signal.—For studying protonated oxygen-bases $HBr-CBr_2F_2$ has the added advantage over HSO_3F in that the acid signal is upfield in the spectrum and far removed from the signal of the conjugate acid; $\delta(^1H, HSO_3F)$ falls around 10—11. However, the position of δ (HBr) is dependent on several factors such as concentration, temperature and the nature of the base (see Table 2). The dependence on concentration and temperature suggests that the acid exists in equilibrium with hydrogen-bonded acid polymers $(HBr)_n$, and the dependence on the base may reflect the differing hydrogen-bonding capabilities of the protonated bases. In these systems there may also be formed the hydrogen dibromide ion, HBr_2^-, which has a downfield shift of δ 10.5,[17] although this is unlikely in view of the lack of a signal in solutions where exchange is slowed down by cooling. Polybromides, $H_nBr_{n+1}^-$, may also be present and in these the averaged proton signal would be upfield.

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