Protonation of Carboxylic Acids by Hydrogen Bromide in Dibromodifluoromethane: Rates of Proton Exchange, Relative Basicities, and the Acidity of HBr–CBr$_2$F$_2$

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Ethanoic, propanoic, butanoic, 2,2-dimethylpropanoic, phenylethanoic, and benzoic acids are fully protonated by HBr–CBr$_2$F$_2$, and at low temperatures (<168 K) separate ^{1}H n.m.r. signals for HBr and RCO$_2$H$_2^+$ are observed. If the temperature is reduced even further then resolution of the two acid proton signals of the latter may be observed. Dichloroethanoic and trichloroethanoic acids are not protonated by this acid system. 2-Chloropropanoic acid may be partly protonated. Line-shape analysis of the n.m.r. spectra at low temperatures has been used to determine the rates of proton exchange between HBr and RCO$_2$H$_2^+$, and in this way an assessment of the relative basicities of the carboxylic acids is obtained. The behaviour of HBr–CBr$_2$F$_2$ is compared with superacid systems.

In previous papers on the acid system HBr–CBr$_2$F$_2$ we have described the protonation of weak bases such as ketones[1] and alcohols.[2] Whether HBr–CBr$_2$F$_2$ can be classed as a superacid is debatable[3] but it does have certain advantages over known superacids. These are the low freezing point of the solvent (132 K) and low oxidising capability of the system. On the other hand the conjugate base, Br$^-$, has a high nucleophilicity in this medium, as shown by the formation of hydrobrominated species with aldehydes[1] and β-diketones.[4]

The acidity of HBr–CBr$_2$F$_2$ is estimated to be in the range -10 to -13 on the H_o scale.[3] Superacids are arbitrarily defined as those with an H_o acidity function of -12 or more.[3] To test the limits of the acidity of HBr–CBr$_2$F$_2$ we have now investigated its ability to protonate a range of very weak bases, the carboxylic acids. The more strongly basic of these are protonated in superacids media such as HSO$_3$F–SbF$_5$,[5,6] HF–SbF$_5$, HF–BF$_3$[8] as well as H$_2$SO$_4$ itself.[9,10] We now report that some carboxylic acids are protonated by HBr–CBr$_2$F$_2$, but not all.

Experimental

Hydrogen bromide (B.D.H.; 99.8%) and CBr$_2$F$_2$ (Aldrich; 99%) were purified by repeated fractional condensation in a vacuum line. A stock solution was prepared by bubbling HBr into CBr$_2$F$_2$ cooled at 195 K (CO$_2$–Me$_2$CO). Solutions were prepared by the addition of a measured volume or weight of the carboxylic acid to the stock solution. CD$_2$Cl$_2$ was added as internal lock and SiMe$_4$ as internal reference.

Ethanoic acid (Fisons AR; glacial) was dried over 4A molecular sieves; propanoic acid and butanoic acid (B.D.H; laboratory grade) were distilled and dried over molecular sieves; 2,2-dimethylpropanoic acid (Fisons SLR) was dried over P$_2$O$_5$ *in vacuo*; phenylethanoic acid (B.D.H laboratory grade) was recrystallised from light petroleum (b.p. 40–60 °C)–diethyl ether and dried over P$_2$O$_5$ *in vacuo*; benzoic acid (Fisons SLR) was recrystallised from benzene and dried over P$_2$O$_5$ *in vacuo*; 2-chloropropanoic acid (Fisons SLR) was distilled under reduced pressure and dried over 4A molecular sieves; dichloroethanoic acid (Fisons AR) was dried over 4A molecular sieves; and trichloroethanoic acid (Fisons AR) was recrystallised from CHCl$_3$ and dried over P$_2$O$_5$ *in vacuo*.

The n.m.r. spectra were recorded with a Bruker WM250 FT spectrometer equipped with a variable-temperature unit, and

Table 1. ^{1}H N.m.r. chemical shifts (ppm) and line-widths (LW) for exchange-proton signals of carboxylic acids in HBr–CBr$_2$F$_2$ at low temperatures.[a]

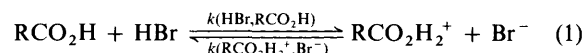|	T_1/K	T_2/K	δ(RCO$_2$H$_2^+$)	LW$_{BH}$/Hz	δ(HBr)	LW$_A$/Hz
CH$_3$CO$_2$H	168		12.9	1 400	−1.97	237
		143	14.2, 15.0		−2.22	
CH$_3$CH$_2$CO$_2$H	158		14.0	675	−2.07	193
		143	14.2, 14.6		−1.95	
CH$_3$(CH$_2$)$_2$CO$_2$H	168		13.10	1 090	−1.29	475
		148	14.20,14.76		−1.95	
(CH$_3$)$_3$CCO$_2$H	153		12.33	1 930	−1.00	413
		140[b]	14.4		−2.11	
PhCH$_2$CO$_2$H	158		13.84	1 350	−2.03	230
		140[b]	14.2		−2.11	
PhCO$_2$H	148		13.5	1 270	−1	v.br.
		143[b]	13.9		−1	

[a] For each carboxylic acid the higher temperature, T_1, is that at which RCO$_2$H$_2^+$ is first recognized as a separate signal; the lower temperature, T_2, is that at which the two acid protons of this species are differentiated. [b] Not resolved into two signals.

operating at 250 (^{1}H) and 62.9 MHz (^{13}C). Table 1 gives the essential data for six acids.

Line-shape analysis was carried out with the program LSHAPE20, a version of LESH that was modified for use with an Aspect 3000 computer.[11]

For the proton-exchange reaction (1), the exchange rates may

$$\text{RCO}_2\text{H} + \text{HBr} \underset{k(\text{RCO}_2\text{H}_2^+,\text{Br}^-)}{\overset{k(\text{HBr},\text{RCO}_2\text{H})}{\rightleftharpoons}} \text{RCO}_2\text{H}_2^+ + \text{Br}^- \quad (1)$$

be determined by measuring the line-broadening of the HBr and RCO$_2$H$_2^+$ signals.[1]

The natural line-width of the HBr signal was measured from the spectrum of a solution of HBr in CBr$_2$F$_2$–CD$_2$Cl$_2$ over the temperature range 268–143 K and an average value of 6.4 Hz was obtained. The natural line-width of the peak due to the hydroxyl protons of RCO$_2$H$_2^+$ cannot be directly measured. The natural line-widths of protonated ethanol and acetophenone have been measured at 40 Hz under similar conditions, and this value was taken as the natural line-width of carboxylic acids studied here.

The overall rate constant k is the average of k_A and k_B, the

Table 2. Rate data for protonation of carboxylic acids at 148 and 153 K.

	[RCO$_2$H]/ mol dm^{-3}	[HBr]/ mol dm^{-3}	log[k-(RCO$_2$H$_2$$^+$,Br$^-$)/ dm^3 mol^{-1}s^{-1}]		σ*[21]
			148 K	153 K	
CH$_3$(CH$_2$)$_2$CO$_2$H	0.279	2.039	a	3.16	−0.115
CH$_3$CH$_2$CO$_2$H	0.129	0.966	3.64	3.83	−0.10
CH$_3$CO$_2$H	0.175	1.675	3.69	4.00	−0.00
(CH$_3$)$_3$CCO$_2$H	0.361	2.039	3.84	4.21	−0.30
PhCH$_2$CO$_2$H	0.154	1.520	4.28	4.37	+0.215
PhCO$_2$H	0.197	0.783	4.30	a	+0.60

^{a} Not observed at this temperature.

exchange rates for the acid and base site respectively. The second-order rate constants for the proton-transfer processes of reaction (1) are related by equations (2) and (3).

$$k(\text{HBr,RCO}_2\text{H}) = k_A/[\text{RCO}_2\text{H}] \qquad (2)$$

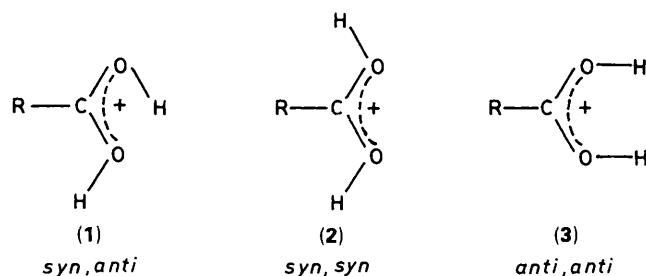$$k(\text{RCO}_2\text{H}_2{}^+,\text{Br}^-) = k_B/[\text{Br}^-] \qquad (3)$$

For the six carboxylic acids listed in Tables 1 and 2, under our reaction conditions (with HBr in excess of RCO$_2$H) reaction (1) in the forward direction is essentially complete and [RCO$_2$H] is immeasurably low. By the same token the equilibrium concentration of Br$^-$ is the same as the original concentration of RCO$_2$H. Hence only $k(\text{RCO}_2\text{H}_2{}^+,\text{Br}^-)$ can be evaluated and the results at 148 and 153 K are reported in Table 2.

Discussion

HBr in CBr$_2$F$_2$ is a sufficiently strong acid to protonate ethanoic, propanoic, butanoic, benzoic, phenylethanoic, and 2,2-dimethylpropanoic acid. When a solution of the carboxylic acid in HBr–CBr$_2$F$_2$ is cooled, a temperature T_1 is reached at which the acid signal resolves into an upfield resonance arising from HBr (at ca. −1 to −2) and a downfield resonance due to RCO$_2$H$_2$$^+$ (at ca. 13–14)[12] and this latter integrates for two protons. For ethanoic, propanoic, and butanoic acids, as the solution is cooled even further to a temperature T_2, the signal due to RCO$_2$H$_2$$^+$ resolves into two broad resonances. The two temperatures, T_1 and T_2, and the peak line-widths are given in Table 1.

The two resolved signals which are observed for ethanoic, propanoic, and butanoic acid at temperature T_2 are due to the two proton environments of the syn,anti conformation (1). The results for benzoic, phenylethanoic, and 2,2-dimethylpropanoic acids do not show this resolution into two acid signals and this can be interpreted in terms of a single conformer in which both protons are equivalent, for example (2) or (3).[13,14] Equally, the single signal may be explained by structure (1) in which there is rapid rotation about the carbon–oxygen bonds on the n.m.r. time-scale.

Di- and tri-chloroethanoic acids are not protonated in HBr–

(1)
syn,anti

(2)
syn,syn

(3)
anti,anti

CBr$_2$F$_2$. At 268 K the ^{1}H n.m.r. spectrum of solutions of these acids in HBr–CBr$_2$F$_2$ shows a single resonance due to rapid exchange between RCO$_2$H and HBr. As the temperature is lowered the peak broadens and at 178 K (for dichloroethanoic acid) and 198 K (for trichloroethanoic acid) resolution into separate peaks due to RCO$_2$H (ca. 12.5, 1 H) and HBr (ca. −2.5) is observed. Monochloroethanoic acid, which would be expected to show behaviour intermediate between that of the more basic acids and di- and tri-chloroethanoic acids, was not sufficiently soluble in HBr–CBr$_2$F$_2$. However 2-chloropropanoic acid was studied. The ^{1}H n.m.r. spectrum in HBr–CBr$_2$F$_2$ showed a single averaged peak for HBr and RCO$_2$H at all temperatures, but the ^{13}C spectrum (see later) gave evidence for partial protonation.

Basicities.—Line-shape analysis was possible on the HBr and RCO$_2$H$_2$$^+$ proton signals between temperatures T_1 and T_2 for ethanoic, propanoic, and butanoic acids, and $< T_1$ for benzoic, phenylethanoic, and 2,2-dimethylpropanoic acids, and the rate data are given in Table 2. In previous work[2] it has been possible to relate the basicity of substituted alcohols, as measured by the rate coefficients for proton exchange, $k(\text{ROH}_2{}^+,\text{Br}^-)$, to the Taft parameters, σ$_I$, of the substituent R.[15] For the six acids for which exchange data could be obtained, values of $k(\text{RCO}_2\text{H}_2{}^+,\text{Br}^-)$ and the σ* values of the substituent R are given in Table 2.

The quantitative basicities of some of the carboxylic acids (pK_{BH^+}) have been reported: ethanoic = −6.2;[16] −6.1;[10] −6.1;[17] propanoic = −6.8;[18] −6.9;[19] −6.3;[10] benzoic = −7.4;[10] −7.3;[20] −7.3;[9] and phenylethanoic = 7.71;[16] −7.6.[20]

Using $k(\text{RCO}_2\text{H}_2{}^+,\text{Br}^-)$ as a guide to the basicity of these acids shows a slightly different ordering. Butanoic acid is the strongest base, followed by propanoic, ethanoic, 2,2-dimethylpropanoic, phenylethanoic, and benzoic acids. Apart from 2,2-dimethylpropanoic acid this order roughly follows the σ* values of the substitutents of R in RCO$_2$H, and therefore σ* proves to be a general guide to the extent to which acids are likely to be protonated in HBr–CBr$_2$F$_2$. For di- and tri-chloroethanoic acids [σ* 1.94 (CHCl$_2$) and 2.65 (CCl$_3$)], protonation is negligible.

Protonation of the carboxylic acids was also studied by observation of the changes in the ^{13}C n.m.r. spectrum. The chemical shift of the carboxylic acid group carbon of trichloroethanoic acid was found at 167.1 ppm at 298 K in CBr$_2$F$_2$, in the absence of HBr. This is a little affected by the presence of HBr, being 168.2 ppm at temperature down to 188 K, and 168.1 ppm below this temperature. Contrasting behaviour was found for 2,2-dimethylpropanoic acid, which was shown to be fully protonated on the basis of the ^{1}H n.m.r. spectrum. In the absence of HBr, the COOH group gave a peak at 186.0 ppm at all temperatures between 298 and 153 K. In the presence of HBr a downfield shift for this carbon was observed and the chemical shift was dependent on temperature. The signal was observed at 187.2 at 238 K, 191.2 (188 K), 192.9 (168 K), and 193.7 ppm (153 K). This downfield shift on cooling has been observed previously for protonated β-diketones.[22] The ^{13}C n.m.r. spectrum of 2-chloropropanoic acid behaves in an intermediate fashion. At 298 K and in the absence of HBr the signal is at 176.8 ppm. With HBr this moves to 177.3 (238 K), 177.6 (188 K), 178.0 (168 K), and 179.1 ppm (153 K). The overall change of 2.3 ppm is significant enough to show that some protonation has occurred.

The least basic carboxylic acids are not always protonated in superacid media. Olah takes the reasonable dividing line between acid and superacid behaviour as that defined by the weakest superacid, 100% H$_2$SO$_4$ with H_o −12. In this medium trichloroethanoic acid is a non-electrolyte, and this is taken as an indication that it is not protonated.[23] Nevertheless

H_2SO_4 can partially protonate dichloroethanoic acid. Again the evidence is based on this compound being a weak electrolyte in H_2SO_4.[24] In this respect sulphuric acid would appear to be marginally stronger as an acid than HBr, which means that $HBr–CBr_2F_2$ just fails to qualify as a superacid according to the accepted definition that superacids are stronger than H_2SO_4. The value of H_o for CBr_2F_2 containing HBr at concentrations of 0.5–1.0 mol dm^{-3} is therefore estimated to be ca. -10 to -12.

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