1,1,1-Trifluoropropan-2-one and 1,1,1-Trifluoropentane-2,4-dione in Hydrogen Bromide–Dibromodifluoromethane; Evidence for the Formation of α-Bromo Alcohols

David R. Clark, John Emsley,* and Frank Hibbert*
Department of Chemistry, King's College London, Strand, London WC2R 2LS

N.m.r. analysis of solutions of 1,1,1-trifluoropropan-2-one (TFP) and 1,1,1-trifluoropentane-2,4-dione (TFPD) in the strong acid system HBr–CBr_2F_2 shows the formation of the 2-bromo alcohol analogues of TFP and TFPD at temperatures below 250 K. In the latter system equilibrium constants for the formation of the bromo alcohol at various temperatures and acid ratios have been measured, from which the enthalpy of formation, $\Delta H^\circ = -25.2$ kJ mol^{-1}, has been calculated. 1,1,1,5,5,5-Hexafluoropentane-2,4-dione (HFPD) does not react to form a bromo alcohol.

In an earlier paper[1] we reported on the behaviour of carbonyl compounds in HBr–CBr_2F_2 solutions, showing that a variety of ketones were protonated by this strong acid system. For example at 183 K pentan-3-one gave clearly resolved ^{1}H n.m.r. signals for HBr and COH^+, from which rate data for protonation and pK(BH^+) were obtained. Propan-2-one, however, was anomalous in that it showed no protonated carbonyl signal even at 144 K. Yet in other acid systems $CH_3C(OH^+)CH_3$ clearly exists.[2–4]

In studying the aldehydes ethanal and 2-methylpropanal, we likewise did not observe a resonance for the conjugate acid proton.[1] These compounds showed significant changes to the aldehyde CH signals such as to prompt us to suggest that 1-bromo alcohols were being formed in these solutions, although no OH signals for RCH(OH)Br were observed even at 150 K. Rapid exchange between this OH and HBr was postulated even at this low temperature.

We now offer firm evidence that α-bromo alcohols can form in HBr–CBr_2F_2. This is the first unequivocal proof of the existence of these compounds, for which we can find no reliable report in the literature.

Experimental

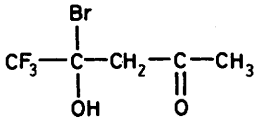
Hydrogen bromide (B.D.H.; 99.8%) and CBr_2F_2 (Aldrich; 99%) were purified by repeated fractional condensation in a vacuum line. A stock solution was prepared by bubbling HBr into CBr_2F_2 cooled at 195 K (CO_2–Me_2CO). The concentration of HBr was determined separately by n.m.r. integration: a weighed amount of 1,1,2,2-tetrachloroethane, sufficient to give a 0.1—0.2 mol dm^{-3} solution, was added to the HBr–CBr_2F_2 solution (0.5 cm^3; containing 0.05 cm^3 CD_2Cl_2 as an internal lock). The single signal of $C_2H_2Cl_4$ at δ 5.87 falls in a region of the spectrum free of other resonances.

TFP (Aldrich; 98%), TFPD (Aldrich; 97%), and HFPD (Aldrich; 96%) were dried over molecular sieves; water content was checked with a Mitsubishi Moisturemeter to ensure a value of less than 50 p.p.m. Solutions for ^{1}H n.m.r. spectrometry were made up by the addition of CD_2Cl_2 (0.05 cm^3) and HBr–CBr_2F_2 (0.45 cm^3) to a measured molar deficiency of the carbonyl compound (by weight). Tetramethylsilane was the internal standard. Solutions for ^{13}C n.m.r. spectrometry were made up with CD_2Cl_2 (0.3 cm^3) and HBr–CBr_2F_2 (2.7 cm^3).

All spectra were recorded with a Bruker WM250 FT spectrometer equipped with a variable-temperature unit, and operating at 250 (^{1}H) and 62.9 MHz (^{13}C). In addition to ordinary broad-band decoupled ^{13}C spectra, distortionless enhancement by polarization transfer (DEPT) 3π/4 pulse sequence was employed. Equilibrium studies were carried out on solutions at temperatures reduced or increased successively by 10 K. After each temperature change an equilibration time of 20—30 min was allowed before the spectrum was recorded.

Results and Discussion

N.m.r. spectroscopy (^{1}H and ^{13}C) of TFPD and TFP in HBr–CBr_2F_2 proved that bromo alcohols are formed under these conditions, and in the case of TFPD the adduct is identified as (**I**).



(**I**)

TFPD in HBr–CBr_2F_2.—Neat samples of TFPD are reported to consist entirely of the enol tautomer,[5] although one study reported 3% of the keto form also.[6] In CBr_2F_2 as solvent, TFPD is 100% enol [see later; equation (1)] with chemical shifts δ 2.19 (CH_3), 5.89 (CH), and 14.39 (OH). By virtue of its low polarity this solvent favours the enol form.[7]

In HBr–CBr_2F_2 at 268 K the signals of the enol are shifted slightly to δ 2.22 (CH_3) and 5.92 (CH), and the OH proton gives a broad peak at 14.5, exchanging slowly with the HBr, the signal of which is upfield of Me_4Si at δ −2.94, and broad. In addition to these recognisable peaks there is a set of signals which we believe are those of 4-bromo-5,5,5-trifluoro-4-hydroxypentan-2-one (**I**): a singlet at δ 2.39 (CH_3), and a pair of doublets at δ 2.99 (J 17.5 Hz) and 3.52 (J 17.5 Hz) due to the CH_2 group and indicating the presence of diastereotopic protons.[8]

The CBr(O*H*) signal was unobserved at 268 K. However, on lowering to 248 K very broad signals were detected at δ *ca.* 7, due to CBr(O*H*). As the temperature was decreased to 168 K this signal increased in intensity, sharpened markedly, and settled at δ 7.77. Indeed the most noticeable change to the spectrum as the temperature decreased was the disappearance of the enol signals with a corresponding rise in the intensity of the bromo alcohol peaks until at 168 K the ratio of enol CH to bromo alcohol OH was 1:14. The reversibility of the chemical equilibrium was shown by raising the temperature, whereupon the enol signals grew in intensity and the bromo alcohol signals decreased.

Table 1. Equilibrium constant $K_{eq.}$ for TFPD + HBr $\rightleftharpoons$ (I) with TFPD:HBr ratio 1:6.00[a]

T/K	[(I)]/[TFPD][b]	$K_{eq.}$/dm^3 mol^{-1}	[(I)]/[TFPD][c]	$K_{eq.}$/dm^3 mol^{-1}
268	0.508	0.510	0.456	0.480
258	0.667	0.714	0.656	0.700
248	1.058	1.15	1.049	1.14
238	1.817	2.03	1.646	1.83
228	3.184	3.64	3.049	3.48
218	4.181	4.82	4.435	5.12
208	6.874	8.03	5.938	6.91
198	8.434	9.89	8.615	10.1
188			11.50	13.6
178			13.29	15.7
168			13.70	16.2

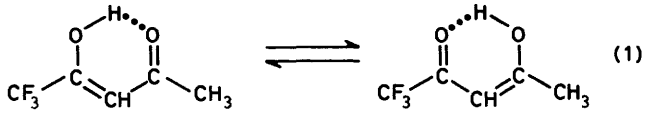
[a] $[HBr]_0$ = 1.002 mol dm^{-3}; $[TFPD]_0$ = 0.167 mol dm^{-3}. [b] Analysis based on integrals of methyl signals. [c] Analysis based on integrals of CH_2 signal of (I) and CH signal of TFPD.

That the chief species in solution at low temperatures is the bromo alcohol (I) was proved by ^{13}C n.m.r. analysis. Spectra in HBr–CBr_2F_2 display a triplet (J_{CF} 357 Hz) centred on δ 90.9 due to the solvent (90.5 in the presence of HBr). This is also the region in which the enol CH signal is found, although the latter is easily identified by running a DEPT spectrum, whereupon the signal of solvent carbon, having no attached protons, is eliminated.

In solution in CBr_2F_2 at 298 K, TFPD displays signals for its five different carbon atoms at δ 24.6 (CH_3), 96.5 (CH), 117.7 (q, CF_3, J_{CF} 282 Hz), 176.8 (q, CF_3C=O, J_{CCF} 36.5 Hz), and 194.4 (CH_3C=O). In HBr–CBr_2F_2 solution at 248 K some of these signals are slightly changed, to δ 24.9, 96.5, 119.4, 177.4, and 194.9. However, the main feature now is the appearance of a new set of resonances consistent with the formation of (I).

At 218 K (I) is the predominant species, apart from the solvent, with signals at δ 32.4 (CH_3), 47.7 (CH_2; DEPT signal inverted), 89.7 [q, CF_3C(OH)Br, J_{CCF} 87 Hz], 120.9 (q, CF_3, J_{CF} = 280 Hz), and 210.8 (CH_3C=O). These signals are exactly those to be expected of a bromo alcohol with the HBr having added across a C=C bond adjacent to the CF_3. Thus a new signal at 89.7 with quartet splitting corresponds to C(OH)Br. Consequently the signal due to the carbonyl next to the methyl group (the acetyl carbonyl) in (I) moves downfield to δ 210.8. The spectrum also now shows a CH_2 signal at δ 47.7, confirmed by the DEPT analysis.

The bromine atom attaches itself to the more electrophilic carbonyl carbon of the molecule, adjacent to the trifluoromethyl group. On the basis of the ^{13}C n.m.r. spectrum of the enol of TFPD, Lazaar and Bauer[9] have shown that the rapid equilibration [equation (1)] favours the tautomer on the left-hand side, with $K_{eq.}$ *ca.* 0.40 in hexane.



(1)

As far as we can ascertain, this is the first time that a bromo alcohol formed by the addition of HBr to a ketone has been positively identified, though it is unstable with respect to the β-diketone at room temperatures. However, the ease with which it establishes an equilibrium with the enol form of TFPD has enabled us to use ^1H n.m.r. spectrometry to analyse solutions and measure the equilibrium constant [for equation (2)].

$$\text{TFPD} + \text{HBr} \overset{K_{eq.}}{\rightleftharpoons} \text{(I)} \qquad (2)$$

The equilibrium constant $K_{eq.}$ was calculated from the integrals of signals due to (I) and TFPD in the ^1H spectra. Both the methyl signals and the CH(enol) and CH_2(bromo alcohol) signals were used to calculate the ratio of concentrations of reactant and product, [(I)]/[TFPD]. In terms of the initial concentrations of reactants, $[HBr]_0$ and $[TFPD]_0$, and this ratio, the value of $K_{eq.}$ is given by equation (3).

$$K_{eq.} = ([(I)]/[TFPD])/\left\{[HBr]_0 - \frac{[TFPD]_0([(I)]/[TFPD])}{1 + [(I)]/[TFPD]}\right\} \qquad (3)$$

The enthalpy for formation of (I), $\Delta H°$/kJ mol^{-1}, was calculated by a linear regression program from the parallel sets of data in Tables 1—3, which gave −23.1 ± 1.1 and −23.6 ± 0.8 from the data of Table 1, −24.2 ± 1.6 and −23.5 ± 1.8 (Table 2), and −28.4 ± 1.1 and −28.3 ± 4.7 (Table 3). In all cases the correlation coefficients were 0.985 or better. The average value of $\Delta H°$ was −25.2 kJ mol^{-1}.

At 298 K the extrapolated value for $K_{eq.}$ is 0.125 dm^3 mol^{-1}, from which $\Delta G°$ = +5.16 kJ mol^{-1} and hence $\Delta S°$ = −102 J K^{-1} mol^{-1} are calculated. As expected the formation of (I) is favoured enthalpically but not entropically.

In Table 3 values of [(I)]/[TFPD] have been obtained for descending as well as ascending temperatures. As the temperature of the system was lowered the OH resonance of the enol tautomer moved upfield from δ 14.5 at 248 K, to 14.3 (208 K), 14.1 (198 K), 14.0 (188 K), 13.7 (178 K), and finally 13.3 (168 K). Below *ca.* 200 K, however, the enol signals were too weak to be integrated. At the very lowest temperatures a second broad signal was also apparent at δ *ca.* 13, which we believe might be due to the protonated bromo alcohol.

The ability of the bromo alcohol (I) to engage in intramolecular hydrogen bonding would seem to be disproved by both the downfield shift of the acetyl carbon signal in the ^{13}C spectrum and the upfield shift of the C(O*H*)Br signal in the ^1H spectrum to δ 7.5 (*cf.* 14.4 in the hydrogen-bonded enol).

TFP in HBr–CBr_2F_2.—The ^1H spectrum of TFP in CBr_2F_2 showed a singlet for the methyl protons at δ 2.37. In the presence of HBr this is shifted to δ 2.42, but even at 268 K the main signal is now due to the bromo alcohol adduct at 2.08, and the broad HBr signal is at −1.94. At this temperature the OH resonance is not seen, but as the temperature is lowered to 178 K this appears as a broad peak at δ *ca.* 6. This sharpens as the temperature is lowered further and shifts so that at 158 K the peak appears at δ 6.49 with peak width 88 Hz (at half height).

Table 2. Equilibrium constant $K_{eq.}$ for TFPD + HBr $\rightleftharpoons$ (I) with TFPD:HBr ratio 1:4.17[a]

T/K	[(I)]/[TFPD][b]	$K_{eq.}$/dm^3 mol^{-1}	[(I)]/[TFPD][c]	$K_{eq.}$/dm^3 mol^{-1}
268	0.174	0.324	0.178	0.332
258	0.297	0.565	0.321	0.613
248	0.506	0.990	0.538	1.11
238	0.855	1.73	0.866	1.75
228	1.27	2.63	1.20	2.48
218	1.87	3.98	1.91	4.07
208	2.10	4.50	2.45	5.30
198	2.38	5.14	2.79	6.08

[a] $[HBr]_0$ = 0.556 mol dm^{-3}; $[TFPD]_0$ = 0.132 mol dm^{-3}. [b] Analysis based on integrals of methyl signals. [c] Analysis based on integrals of CH_2 signal of (I) and CH signal of TFPD.

Table 3. Equilibrium constant $K_{eq.}$ for TFPD + HBr $\rightleftharpoons$ (I) with TFPD:HBr ratio 1:2.01[a]

T/K	[(I)]/[TFPD][b]	$K_{eq.}$/dm^3 mol^{-1}	[(I)]/[TFPD][c]	$K_{eq.}$/dm^3 mol^{-1}
268	0.567	0.259	0.597	0.329
258	0.894	0.524	0.923	0.543
248	1.41	0.892	1.43	0.901
238	2.02	1.36	2.14	1.44
228	3.72	2.74	4.24	3.14
218	6.94	5.51	8.17	6.59
208		Enol signals too small for integration		
218	8.35	6.75	8.71	7.06
228	3.98	2.97	4.52	3.42
238	2.14	1.31	2.41	1.67
248	1.39	0.877	1.46	0.929
258	0.855	0.497	0.923	0.543
268	0.546	0.297	0.605	0.334

[a] $[HBr]_0$ = 2.234 mol dm^{-3}; $[TFPD]_0$ = 1.116 mol dm^{-3}. [b] Analysis based on integrals of methyl signals. [c] Analysis based on integrals of CH_2 signal of (I) and CH signal of TFPD.

Table 4. Equilibrium constant $K_{eq.}$ for TFP + HBr $\rightleftharpoons$ $CF_3CBr(OH)CH_3$ (II) with TFP:HBr ratio 1:5.14[a]

T/K	[(II)]/[TFP][b]	$K_{eq.}$/dm^3 mol^{-1}
268	4.03	2.13
258	7.44	4.00
248	11.42	6.20

[a] $[HBr]_0$ = 2.243 mol dm^{-3}; $[TFP]_0$ = 0.436 mol dm^{-3}. [b] Analysis based on integrals of methyl signals.

Sharpening of the OH signal is matched by a decrease in width of the HBr peak. At 158 K the equilibrium has shifted completely in favour of the adduct and the ketone is no longer detectable. The values of the equilibrium constant for adduct formation are given in Table 4; the results show that this is more favoured than for TFPD at the same temperature.

Again the identity of the suspected 1,1,1-trifluoro-2-bromopropan-2-ol was proved conclusively by ^{13}C n.m.r. spectroscopy. TFP itself has resonances at δ 23.4 (CH_3), 116.2 (q, CF_3, J_{CF} 291 Hz), and 188.5 (q, C=O, J_{CCF} 36 Hz). In the presence of HBr other signals were observed and at 208 K these had entirely replaced those of TFP. The n.m.r. spectrum was then consistent with $CF_3C(OH)BrCH_3$; δ 27.2 (CH_3), 86.5 [q, C(OH)Br, J_{CCF} 35 Hz], and 122.2 (q, CF_3, J_{CF} 282 Hz). The nature of the carbon atoms of these species was confirmed by their DEPT spectra.

HFPD in HBr–CBr_2F_2.—The ^1H spectra of a solution of HFPD (0.272 mol dm^{-3}) in a 2.346 mol dm^{-3} solution of HBr in CBr_2F_2 were monitored from 268 K down to 158 K. The spectrum remained unchanged from that of HFPD, which shows only two signals at δ 6.37 and 12.87 due to CH and OH, respectively, of the enol tautomer in the absence of HBr. In the presence of HBr, and even as high as 268 K these protons signals persisted, showing there to be slow exchange between the HBr and the enol proton. At 228 K both the enol OH and HBr signals were very sharp at δ 12.95 and −2.85, respectively, and indicating no exchange. They remained sharp down to the lowest temperatures. At no point was there any indication of the formation of a 2-bromo alcohol.

The behaviour of HFPD is unexpected on three counts that may in some way be related. First there is no formation of a bromo alcohol; secondly, exchange between the enol tautomer proton of this molecule and the excess of HBr is much slower than in the case of TFPD; and thirdly the chemical shift of the enol form is at higher field than observed for TFPD. These observations may all reflect different behaviour of the hydrogen bonds of TFPD and HFPD, and this is being further investigated.

Acknowledgements

We thank the Conoco Education Trust for a grant (for D. R. C.).

References

1 J. Emsley, V. Gold, and M. B. J. Jais, *J. Chem. Soc., Perkin Trans. 2*, 1982, 881.
2 G. A. Olah and C. U. Pittman, *J. Am. Chem. Soc.*, 1966, **88**, 3310.
3 M. Brookhart, G. C. Levy, and S. Winstein, *J. Am. Chem. Soc.*, 1967, **89**, 1735.

4 V. Gold, K. Laali, K. P. Morris, and L. Z. Zdunek, *J. Chem. Soc., Perkin Trans. 2*, 1985, 865.
5 J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, 1964, **86**, 2105.
6 G. Allen and R. A. Dwek, *J. Chem. Soc. B*, 1966, 161.
7 J. Emsley and N. J. Freeman, *J. Mol. Struct.*, 1987, **161**, 193.
8 W. Kemp, 'NMR in Chemistry, a Multinuclear Introduction,' Macmillan, London, 1986.
9 K. I. Lazaar and S. H. Bauer, *J. Phys. Chem.*, 1983, **87**, 2411.

Received 30*th September* 1987; *Paper* 7/1742