Solutions of HBr in Sulpholane

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Solutions of HBr in $C_4H_8SO_2$ (2,3,4,5-tetrahydrothiophen 1,1-dioxide; sulpholane) are brown in colour, due to the presence of Br_2. Infrared and u.v. investigations have established that equilibrium is set up in the system with

$$C_4H_8SO_2 + 2HBr \overset{K}{\rightleftharpoons} C_4H_8SO + Br_2 + H_2O$$

$K = 2.4 \times 10^{-5}$ at 20 °C ($\Delta H = -55$ kJ mol^{-1} and $\Delta S = -275$ J K^{-1} mol^{-1}). Proton n.m.r. observations of HBr–$C_4H_8SO_2$ solutions show that protonation of the solvent occurs. The addition of H_2O to such solutions leads to unusual n.m.r. spectra that indicate only slow exchange of H between $C_4H_8SO_2H^+$ and H_2O.

BAGSTER and his collaborators[1,2] studied solutions of HBr in liquid SO_2 and the effect of the addition of water on the electrical conductivity. They explained their observations in terms of H_3O^+. We have been interested in the further study of these systems, especially by n.m.r. spectroscopy. However, liquid SO_2 is not a good solvent for H_2O especially at the low temperatures required to observe H_3O^+ by n.m.r. techniques. Another complication is apparent, in that solutions of HBr in liquid SO_2 turn brown; a fact that was disregarded by the early workers.

Sulpholane is a polar non-acidic solvent[3] like SO_2 but with the advantage of being completely miscible with H_2O. It is reputedly stable to acids,[3] but this observation rests on a report that refluxing a solution of 93% aqueous H_2SO_4 in sulpholane for 5 h caused only 11% decomposition.[4] As a solvent, sulpholane has the disadvantage of a high m.p. (28.45 °C) but its cryoscopic constant is large[5] so that most solutions are liquid at room temperatures. Its similarity to liquid SO_2 in other respects is well known.[6] An unexpected similarity, now reported, is the brown colouration which develops on adding pure HBr to the solvent. This colour appears within minutes in sulpholane at room temperature. A pale yellow colour can be seen within minutes of adding HBr to liquid SO_2 at −10 °C and this darkens slowly on standing over a period of several hours.

The study of HBr in sulpholane prompted this report.

EXPERIMENTAL

Sulpholane (B.D.H.) was dried over $CaCl_2$ at 40 °C and then distilled under reduced pressure. Gaseous HBr (B.D.H.) was purified by fractional condensation. 2,3,4,5-Tetrahydrothiophen 1-oxide (Aldrich), C_4H_8SO, was used without purification. The i.r. spectra were measured on a Perkin-Elmer 457 spectrometer (0.05-mm cell), u.v. spectra on either a Perkin-Elmer R12B (60 MHz) or a Bruker HFx (90 MHz) spectrometer. A Copenhagen Radiometer G-202B pH meter with glass electrode was used to measure pH.

Solutions of HBr in sulpholane were prepared by passing the gas into the molten solvent. A 0.4 mol dm^{-3} HBr solution could be held at 5 °C without solidification. The concentration of C_4H_8SO in such solutions was measured by observing the absorption maximum at 226 nm and comparing it with a calibration curve for solutions of the sulphoxide in sulpholane. The equilibrium constant values, K, are listed in Table 1.

TABLE 1

Values of 10^5K for reaction (1)

	Concentration HBr in sulpholane/mol dm^{-3}				
θ_c/°C	0.4	0.8	1.2	1.6	2.0
5	17.6	6.7	8.3	7.3	7.9
10	10.0	6.1	7.5	6.5	5.6
15	3.9	5.5	5.6	5.3	3.4
20	2.9	2.8	2.6	3.2	2.3
25	2.3	2.0	1.4		
30	1.7	1.2	1.3		

The Reaction of 2,3,4,5-*Tetrahydrothiophen* 1-*Oxide, Water, and Bromine.*—To a mixture of C_4H_8SO (2.60 g, 0.025 mol) and H_2O (0.45 g, 0.025 mol), Br_2 (4.00 g, 0.025 mol) was added. The mixture became warm and was left at room temperature for 10 h. On treatment with solid $Na_2[CO_3]$ the solution effervesced and the bromine colour became noticeably paler. The solution was then filtered to remove solid salts. The amount of unreacted C_4H_8SO (0.087 g, 0.000 93 mol) was measured by u.v. The conversion to $C_4H_8SO_2$ was 90.7%.

RESULTS AND DISCUSSION

The Oxidation–Reduction Equilibrium (1).—The unreported, and unexpected, observation of a brown colouration, forming within a few minutes of dissolving HBr gas in sulpholane, at first suggested the presence of an oxidising impurity. However, the same behaviour was found after purification of the solvent. It was therefore concluded that the oxidising action of sulpholane itself is responsible, *i.e.* equilibrium (1) is established in

$$C_4H_8SO_2 + 2HBr \rightleftharpoons C_4H_8SO + Br_2 + H_2O \quad (1)$$

this system. The brown colour is due to the presence of bromine, presumably in the form of its charge-transfer complex to the sulphoxide.

The presence of Br_2 and of the sulphoxide in solutions prepared from HBr and sulpholane were demonstrated by u.v. spectroscopy. Sulpholane itself does not absorb between 190 and 400 nm, nor does HBr in inert solvents, but a 0.002 4 mol dm^{-3} solution of HBr in sulpholane showed two absorption maxima at 226 and 278 nm. An identical spectrum, but with a more intense 226 nm band, was produced by mixing a 3.14×10^{-6} mol dm^{-3} Br_2 solution in sulpholane with an excess of 15.7×10^{-6} mol

dm^{-3} C_4H_8SO solution in sulpholane. The addition of water to the system, to make it directly comparable to the right-hand side of (1), had no effect on the wavelengths. The 226 nm band is attributed to C_4H_8SO presumably as its charge-transfer complex $C_4H_8SO{\cdot}Br_2$, analogous to the complex $C_4H_8SO{\cdot}I_2$ which in CCl_4 solution has a maximum at 279 nm.[7] (The use of CCl_4 precludes measurement of wavelengths below 260 nm.)

If equilibrium (1) represents the true state of affairs in these solutions then H_2O should also be detectable. The i.r. spectrum of sulpholane in the region 1 000—4 000 cm^{-1} and of a 0.17×10^{-4} mol dm^{-3} H_2O solution clearly showed that the water bands at 3 600, 3 530, and 1 646 cm^{-1} could be observed. The spectrum of 0.044 mol dm^{-3} HBr in sulpholane also showed these H_2O peaks. The formation of C_4H_8SO could not be proved under these conditions owing to overlapping sulpholane absorptions. However, solutions of sulpholane in benzene, with HBr in excess, clearly showed the decrease in intensity of the sulpholane absorptions at 1 410 and 900 cm^{-1} and the concurrent emergence of sulphoxide bands at 785 and 815 cm^{-1}. Water itself separated out from these solutions.

The equilibrium constant K for (1) was calculated by measuring the concentration of C_4H_8SO from the u.v. peak at 226 nm. The results for a range of HBr concentrations and temperatures are given in Table 1, based on $K = [C_4H_8SO][Br_2][H_2O]/[C_4H_8SO_2][HBr]^2$. This equation simplifies to $K \simeq [C_4H_8SO]^3/[C_4H_8SO_2]([HBr]_0 - 2[C_4H_8SO])^2$ where $[HBr]_0$ is the original concentration of HBr. A plot of ln$K$ against $1/T$ is shown in the Figure from which a linear least-squares fit gives $\Delta H = -55$ kJ mol^{-1} (standard error 4 kJ mol^{-1}) for the (forward) reaction (1), and $\Delta S = -275$ J K^{-1} mol^{-1} (standard error 14 J K^{-1} mol^{-1}).

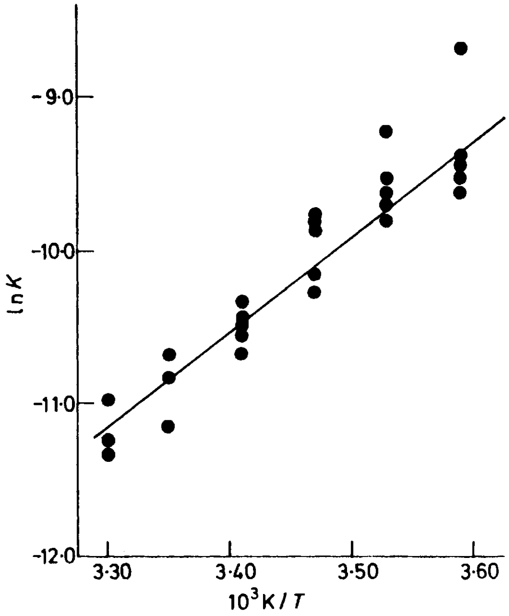
The oxidation of sulphoxide by bromine appears not to have been reported previously.[8] Indeed quite the reverse; heating a 10 : 1 ratio of C_4H_8SO : Br_2 at 100 °C for 3 days in a sealed tube produced a 54% yield of C_4H_8S,[9] and heating a mixture of 1 : 1 C_4H_8SO : Br_2 in liquid SO_2 and MeCN at 80 °C for 2 h in a sealed tube gave a 19% yield of the sulphide.[10] However, bromine in the presence of *N*-bromosuccinimide and pyridine effects bromination of C_4H_8SO at the α carbon.[11] Moreover sulphides and sulphoxides can be oxidized to sulphones by Na[OCl] [12] and Cl_2.[13]

A 0.01 mol dm^{-3} solution of bromine water has a pH of 4.70. Addition of an equivalent amount of C_4H_8SO causes a drop in pH over a period of 20 min to a stationary value of 4.15 and the solution becomes colourless. A 0.001 mol dm^{-3} solution of hydrobromic acid on addition of excess of sulpholane shows a rise in pH from 3.0 to 3.7 during a similar time interval. Both of these observations can be interpreted in terms of equilibrium (1), taking into account the greater basicity of C_4H_8SO ($pK_{HB^+} = -1.49$) [14] compared to the very weak basicity of $C_4H_8SO_2$ ($pK_{HB^+} = -12.88$).[15]

Equilibrium (1) can also be approached from the right-hand side as a chemical reaction of C_4H_8SO, Br_2, and H_2O in a 1 : 1 : 1 molar ratio. This gave a 91% oxidation to $C_4H_8SO_2$ at room temperature after 10 h. The equilibrium constant K for (1) calculated from this reaction, the details of which are given in the Experimental section, is 1.4×10^{-5} in agreement with the values of Table 1.

Reduction of sulphones to sulphoxides, which our observations suggest to be feasible by the use of hydrogen bromide, has not hitherto been thought to be a practically useful reaction. Most reducing agents, such as $Li[AlH_4]$, capable of reducing sulphones reduce them to sulphides or cleave the C–S bond.[16]

The Protonation of Sulpholane.—The ^1H n.m.r. spectrum of sulpholane in the very strong ' magic acid ' system HSO_3F–SbF_5, diluted with SO_2ClF, did not reveal an additional new signal for the $C_4H_8SO_2H^+$ ion, even at −80 °C.[17] On the basis of a downfield chemical shift of 1.15 p.p.m. of the α-H atoms, Olah *et al.*[17] concluded that protonated sulpholane was formed. On the other hand from a chemical shift at 6.5 p.p.m. the authors concluded that sulphoxides in ' magic acid ' were protonated not at oxygen but at sulphur.



Plot of ln K against $1/T$ for equilibrium (1)

Is HBr in sulpholane a sufficiently strong acid to protonate the solvent? Low-temperature observations are ruled out because of the high m.p.s. In Table 2 are listed the ^1H n.m.r. signals of the acid proton at different concentrations of HBr. The oxidation–reduction equilibrium (1) does not interfere significantly with these observations. At all concentrations the signal is downfield of $SiMe_4$, whereas in non-polar solvents, such as CCl_4, the signal for HBr is upfield of $SiMe_4$, *e.g.* δ(HBr, 2.0 mol dm^{-3} HBr in CCl_4) = −3.28 p.p.m.

The signal in sulpholane is seen to shift downfield on dilution. This is explicable in terms of protonation of the solvent (2) and rapid proton exchange between C_4H_8-

TABLE 2

Positions of ^1H n.m.r. signals for solutions of HBr and of H_2O in sulpholane

HBr		H_2O	
[HBr]/mol dm^{-3}	δ/p.p.m.	[H_2O]/mol dm^{-3}	δ/p.p.m. *
0.1	7.81	0.05	2.52
0.25	6.74	0.22	2.52
0.50	5.78	0.44	2.52
0.75	3.59	0.66	2.58
1.00	3.18	1.11	2.68
1.50	2.61	1.55	2.74
2.00	2.45	2.00	2.78
2.50	2.05	2.22	2.84
3.00	1.36		

* Downfield from $SiMe_4$.

SO_2H^+ and HBr. Ionization of HBr increases with dilution and at infinite dilution the position of the signal

$$C_4H_8SO_2 + HBr \rightleftharpoons C_4H_8SO_2H^+ + Br^- \qquad (2)$$

should correspond to protonated sulpholane, downfield at *ca.* 10 p.p.m. At higher concentrations the position of the signal represents a weighted average.

An alternative deshielded environment that can be envisaged is the bibromide ion, $\delta(HBr_2^-) = 10.5$ p.p.m.,[18] but the concentration of this should *decrease* on dilution and δ(HBr) should shift upfield.

The compound $HSbCl_5$ has been reported to be a strong acid in sulpholane as shown by its n.m.r. and conductivity behaviour,[19] and so has HBF_4.[20] Most other acids including HCl, $HClO_4$, $H_2S_2O_7$, and HSO_3F (by itself) [21] have been stated to be undissociated. HBr has been included in this category.[20] However, our ^1H n.m.r. data suggest that it is in fact a moderately strong acid. This conclusion corroborates the unusually high acidity of HBr in CF_2Br_2 which has recently been demonstrated by us.[22] Dissolution of water or alcohols in this medium gave a solution in which separate signals for HBr and ROH_2^+ (R = H, Me, or Et) were observed at temperatures below −100 °C (*i.e.* proton exchange is relatively slow).

By contrast with this behaviour of alcohols, the addition of $C_4H_8SO_2$ to solutions of HBr in CF_2Br_2 did not produce a separate signal for the $\overset{+}{O}H$ group in protonated sulpholane. The only acid proton observed at room temperature is the upfield signal of HBr. Even cooling to low temperature showed no $C_4H_8SO_2H^+$ peak; the irregular variation in chemical shift and broadness of the signal (Table 3) suggest the occurrence of kinetically significant changes in the environment of protons but this is probably due to exchange among $(HBr)_n$ species or polymerization–depolymerization reactions. The low polarity of solvent CF_2Br_2 keeps equilibrium (2) well to the left-hand side.

The addition of H_2O to HBr in sulpholane produces a remarkable ^1H n.m.r. spectrum.* An equimolar concentration of H_2O and HBr in sulpholane eventually gives an acidic proton singlet at 9.77 p.p.m., but only after a complex series of other signals in this region has been observed. On adding H_2O a singlet at 9.72 p.p.m. appears immediately, to be joined after 1.25 min by a second signal at 9.86 p.p.m. and after 3.4 min by a third signal at 9.68 p.p.m. After 6 min these three peaks, of roughly the same intensity, begin to coalesce and by 9 min are seen as a singlet at 9.77 p.p.m. These observations are hard to explain and merit further investigation.

The most likely effect of adding H_2O to HBr in sulpholane is to remove all the protons from HBr to form H_3O^+ and we see the oxonium signal. This, at 9.72 p.p.m. is in the expected region, reported to be at δ 9.3—10.8 p.p.m. in HSO_3F–SbF_5–D_2O–liquid SO_2.[23] The transfer of protons between this ion and $C_4H_8SO_2$ may be slow on the n.m.r. time scale even at 30 °C so that we see separate signals for the environments $H_2\overset{+}{O}$–H $\cdots$ O_2-SC_4H_8 and $H_2O \cdots$ H–$\overset{+}{O}_2SC_4H_8$. It may then be that $C_4H_8SO_2H^+$ acts as a catalyst for subsequent proton exchange so that the signals for these various species and H_3O^+ coalesce.

TABLE 3

Hydrogen-1 n.m.r. data for HBr + $C_4H_8SO_2$ in CF_2Br_2*

θ_c/°C	δ/p.p.m.	Signal	θ_c/°C	δ/p.p.m.	Signal
−30	−2.33	Sharp	−90	−2.11	Broad (37 Hz)
−50	−1.85	Sharp	−100	−2.07	Less broad (23 Hz)
−60	−1.77	Broadens (22 Hz)	−110	−1.85	Sharper
−70	−1.74	Broad (33 Hz)	−120	−1.70	Sharper
−80	−1.85	Very broad (53 Hz)	−130	−1.52	Sharper

* Only upfield signal data given; $C_4H_8SO_2$ protons at usual position (α-H = 3.14 and β-H = 2.33 p.p.m.). Solution was 3×10^{-3} in HBr and 1×10^{-3} mol dm^{-3} in $C_4H_8SO_2$.

By analogy with the HBr–sulpholane system the HBr–SO_2 system should exhibit equilibrium (3). Although SO can be produced from SO_2 and sulphur vapour

$$SO_2 + 2HBr \rightleftharpoons SO + Br_2 + H_2O \qquad (3)$$

in a glow discharge at 0.5 Torr † and 120 °C it is a transient species even under the most favourable conditions. It has a half-life of less than 0.005 s at 0.001 Torr and 20 °C. Disproportionation to S_2O and SO_2 occurs in the gas phase.[24] In solution we would expect it to react with either HBr or SO_2. Evaporation of HBr–SO_2 solutions leaves behind an involatile material, which might be the product of such a reaction but which has yet to be identified.

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* The signal for H_2O alone in sulpholane is given in Table 2.

† Throughout this paper: 1 Torr = (101 325/760) Pa.

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