Hydrogensulphates of Silver(I) and some Transition-metal Cations

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Pure $Ag[HSO_4]$ cannot be made by fusing mixtures of $Ag_2[SO_4]$ and H_2SO_4 in accord with a derived phase diagram, but can be precipitated from $Ag[O_2CCF_3]$ and H_2SO_4 in CF_3CO_2H. Tetra- and hepta-solvates result from contacting $Ag_2[SO_4]$ and H_2SO_4 in acetonitrile; the rate of solution of the sulphate controls the overall reaction. Hydrogensulphates of di- and tetra-solvated transition-metal ions (Cu^{I}, Cu^{II}, Zn^{II}, Cd^{II}, Mn^{II}, Fe^{II}, and Ni^{II}) can be made by metathesis of their halides and $Ag[HSO_4]$ in MeCN, or by attacking the metals with dilute solutions of H_2SO_4 in MeCN. The inability to desolvate these salts without loss of H_2SO_4 is correlated with the strength of the M^{n+}–NCMe interaction. The solubilities of $Ag[HSO_4]$ in organic solvents are explained in terms of depolymerization of hydrogen-bonded anions.

HYDROGENSULPHATES of transition-metal ions cannot be obtained from sulphuric acid because of the low solubility of their sulphates in this acid. Even when the sulphate is soluble it is difficult to isolate pure hydrogensulphates from the viscous medium and this is reflected in previous analytical data.[1,2] Hence the tendency has been to characterize hydrogensulphates by their colligative and spectral properties in solution. Because we are interested in pursuing the correspondence between fluoro- and hydrogen-sulphates, which was indicated by the almost identical formation enthalpies of corresponding salts,[3] we have investigated other preparative media. The prime requirement for such media is the ability to suppress the second deprotonation of H_2SO_4. Trifluoroacetic acid seemed a possible medium since Fujioka and Cady [4] isolated mixtures of sulphates and hydrogensulphates when excess of H_2SO_4 was added to metal trifluoroacetates in CF_3CO_2H. Another possibility was methyl cyanide in which Kolthoff *et al.*[5,6] showed that the first dissociation constant of H_2SO_4 is 10^{18} times the second, compared with a ratio of $10^4 : 1$ in water. Other aprotic solvents such as dimethyl sulphoxide appear less favourable. There was also the possibility that fluorosulphuric acid could be used as a medium because, in prolonged displacement reactions with metal sulphates, it was observed that the fluorine content of the fluorosulphates isolated was low even when the metal content was nearly correct indicating partial replacement of F by OH as H_2SO_4 was released.[7]

We are especially interested in silver(I) hydrogensulphate because of its possible application as a metathetical and catalytic reagent. The pure salt had not been isolated prior to this work, although Nazarova [8] obtained a salt of the correct composition from fused mixtures of silver(I) sulphate and H_2SO_4. The salt isolated by Schultz [1] by recrystallizing $Ag[SO_4]$ in H_2SO_4 was impure and contained appreciable extra acid.

EXPERIMENTAL

Trifluoroacetic acid, CF_3CO_2H, was dried by heating under reflux with P_4O_{10} before fractional distillation. Methyl cyanide, MeCN, was finally dried with CaH_2 before fractionation. Sulphuric acid was adjusted to a minimum conductivity with oleum. Materials were manipulated under dry nitrogen in a glove-box or in special glass vessels. Silver was determined by Volhard's titration, acidic hydrogen by alkalimetry, sulphate as $Ba[SO_4]$, and metals gravimetrically or by ethylenediaminetetra-acetic acid titrimetry.

Preparation of Silver(I) *Hydrogensulphate.—Attempt in melt.* Equimolar amounts of $Ag_2[SO_4]$ and H_2SO_4 were sealed in a glass tube. Neither heating to 150 °C nor long anneals at 130 °C eliminated the small amount of fine white powder which remained when the bulk melted at 110 °C. The crystallized melt extracted with MeCN left the fine powder which analyzed close to the $Ag_2[SO_4]$ composition. The solution gave a $H^+ : Ag^+$ ratio of 1.13 : 1, intermediate between those expected for $Ag_2[SO_4] : 1$ and 2 H_2SO_4. Repeat experiments with slight temperature variations gave similar results.

In CF_3CO_2H. Equal volumes of 5M-$Ag[O_2CCF_3]$ and 5M-H_2SO_4 were mixed.† Most of the solution was decanted from the white precipitate and the rest removed *in vacuo* at room temperature (Found: Ag, 52.9; SO_4, 47.0. Calc. for $Ag[HSO_4]$: Ag, 52.6; SO_4, 46.9%). Less vigorously dried reactants gave products contaminated with $Ag_2[SO_4]$. [Silver(I) fluorosulphate can be made similarly using HSO_3F in place of H_2SO_4.]

In MeCN. A 1M solution of H_2SO_4 in MeCN was added to an excess of solid $Ag_2[SO_4]$ in MeCN and left for 4 d. [Pellets of dried molecular sieve (Linde 4A) were added to maintain dryness.] The filtered solution had a $Ag^+ : H^+ : [SO_4]^{2-}$ ratio of 1.000 : 0.991 : 1.0035. The solution was concentrated by vacuum evaporation until crystallization started. This cooled the solution below 10 °C and if this temperature were not exceeded, colourless crystals of a heptasolvate separated (Found: H, 0.20; Ag, 21.9; SO_4, 19.6. Calc. for $Ag[HSO_4]\cdot 7NCMe$: H, 0.20; Ag, 21.9; SO_4, 19.5%). These crystals effluoresced at room temperature and a tetrasolvate was isolated after a quick exposure *in vacuo* (Found: H, 0.25; Ag, 30.0; SO_4, 27.4. Calc. for $Ag[HSO_4]\cdot 4NCMe$: H, 0.25; Ag, 29.2; SO_4, 26.6%). This compound could be desolvated *in vacuo* to $Ag[HSO_4]\cdot$

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† 1M = 1 mol dm^{-3}.

[1] C. Schultz, *Pogg. Ann.*, 1868, **133**, 137.

[2] J. Kendall and A. W. Davidson, *J. Amer. Chem. Soc.*, 1921, **43**, 979.

[3] G. W. Richards and A. A. Woolf, *J. Chem. Soc.* (*A*), 1968, 470.

[4] G. S. Fujioka and G. H. Cady, *J. Amer. Chem. Soc.*, 1957, **79**, 2451.

[5] I. M. Kolthoff and M. K. Chantooni, *J. Amer. Chem. Soc.*, 1968, **90**, 5961; 1961, **91**, 25.

[6] I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, *J. Amer. Chem. Soc.*, 1961, **83**, 3927.

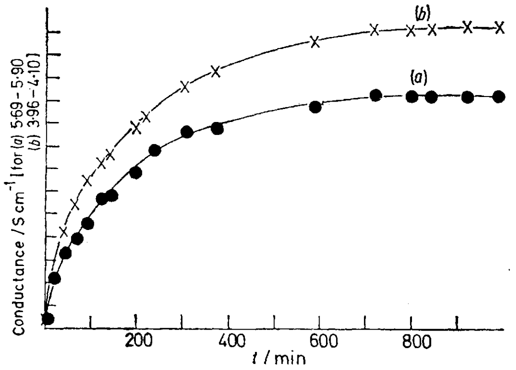
[7] A. A. Woolf, *J. Chem. Soc.* (*A*), 1967, 355.

[8] Z. N. Nazarova, *J. Gen. Chem.* (*U.S.S.R.*), 1948, **18**, 430.

1.3NCMe. Beyond this stage it decomposed to $Ag_2[SO\ ]$ and H_2SO_4.

A more rapid preparation of a $Ag[HSO_4]$ solution was effected by taking an incompletely reacted mixture still containing unchanged H_2SO_4 and evaporating until the cooled solution deposited the heptasolvate. Crystals were isolated by decanting the mother liquor and were recrystallized with fresh MeCN. {Initial solution composition ($Ag[HSO_4]$ and H_2SO_4), 0.703 and 0.068; first recrystallization, 0.362 and 0.017; second recrystallization 0.304 and 0.002 mol kg^{-1}.}

Rate of Equilibration of $Ag_2[SO_4]$ *and* H_2SO_4 *in* MeCN.—This was followed conductimetrically in solution at 24 °C because the conductivity increased as the weakly acidic H_2SO_4 solution was replaced by the strong electrolyte $Ag[HSO_4]$. Two solutions were compared at nearly equal $Ag_2[SO_4] : H_2SO_4$ ratios but with one acid concentration more than twice the other: (*a*) 1.852 g $Ag_2[SO_4]$ in 28.57 g of 0.1281 mol kg^{-1} H_2SO_4 or 5.95 mmol $Ag_2[SO_4]$, $Ag_2[SO_4] : H_2SO_4 = 1.66 : 1$; and (*b*) 2.98 mmol $Ag_2[SO_4]$, $Ag_2[SO_4] : H_2SO_4 = 1.78 : 1$. The results are plotted in the Figure.



Conductance against time plots for the system $Ag_2[SO_4]$–H_2SO_4 in MeCN. For conditions of (*a*) and (*b*) see text

The validity of the method was checked by measurements in $Ag[HSO_4]$ and $Ag[HSO_4]$–H_2SO_4 mixtures. Unstirred reaction rates were measured for comparison {6.34 mmol $Ag_2[SO_4]$ ($Ag_2[SO_4] : H_2SO_4 = 1.53 : 1$) was 90% depleted in H_2SO_4 in 3 d at 22 °C; 1.70 mmol $Ag_2[SO_4]$ ($Ag_2[SO_4] : H_2SO_4 = 1.53 : 1$) was 98% depleted in 4 d from analysis of the solutions}.

Properties of $Ag[HSO_4]$.—In MeCN at 25.0 °C the following conductivities were obtained: 96.87 (0.037 03); 108.66 (0.022 97); 125.26 (0.010 76); 130.48; (0.008 779); 132.43 (0.008 056); 136.80 (0.006 312); 151.71 (0.002 709); and 158.95 S cm^2 mol^{-1} (0.001 407M). Extrapolation of the λ against $c^{\frac{1}{2}}$ curve gave a value of 186.0 S cm^2 mol^{-1} at infinite dilution.

Solubilities in MeCN. Solutions, saturated by pumping off MeCN, were left to equilibrate. Large crystals of the heptasolvate were formed from which the saturated soltions could be decanted and analyzed (Found: 3.68 at −10.0; 6.17 at 0; 6.98 at 1.50; and 11.86 wt. % $Ag[HSO_4]$ at 9.90 °C.

Thermal stability. The weight loss of the anhydrous salt was followed on a thermobalance (Stanton) under dry nitrogen. At a heating rate of 5 °C min^{-1} there was a continuous loss from 70 to 460 °C corresponding to equation (1). At the slower rate of 1 °C min^{-1} the sample, which again started to lose weight at 70 °C, had lost $\frac{1}{2}$ H_2O by 220 °C. An i.r. spectrum of the residue corresponded to

$$Ag[HSO_4] \longrightarrow \tfrac{1}{2}Ag_2[SO_4] + \tfrac{1}{2}H_2O + \tfrac{1}{2}SO_3 \quad (1)$$

that of a disulphate. The silver(I) disulphate was isolated by maintaining the temperature at 175 °C when the sample reached constant weight after 8 h. Further decomposition occurred at 315 (2.5 h) and 920 °C.

$$Ag[HSO_4] \xrightarrow{170\ ^\circ C} \tfrac{1}{2}Ag_2[S_2O_7] + \tfrac{1}{2}H_2O \quad (2)$$

$$\tfrac{1}{2}Ag_2[S_2O_7] \xrightarrow{315\ ^\circ C} \tfrac{1}{2}Ag_2[SO_4] + \tfrac{1}{2}SO_3 \quad (3)$$

$$\tfrac{1}{2}Ag_2[SO_4] \xrightarrow{920\ ^\circ C} Ag + \tfrac{1}{2}SO_3 + \tfrac{1}{4}O_2 \quad (4)$$

Metathetical reactions. A solution of $Ag[HSO_4]$ (0.4 mol kg^{-1}) in MeCN was used. Silver(I) hydrogensulphate (2.5 mmol) and CuCl (2.5 mmol) were mixed. Silver(I) chloride was quantitatively precipitated and filtered off. Small white crystals were obtained by vacuum evaporation of the filtrate. These were dried on filter paper in the glove-box and analyzed as $Cu[HSO_4]$·4NCMe. Copper(II) chloride (1.0 mmol) was mixed with $Ag[HSO_4]$ (2.0 mmol) in MeCN (300 cm^3). The blue Cu^{II} salt partly precipitated with the AgCl and could be redissolved in more MeCN. The remaining solution was evaporated and crystallization yielded $Cu[HSO_4]_2$·4NCMe. (An alternative route to these salts was to equilibrate $Cu[SO_4]$ with H_2SO_4 in MeCN to obtain the Cu^{II} salt and to add Cu to the solution to obtain the Cu^{I} salt.)

Cadmium(II) iodide (4.1mmol) in MeCN was added to an equivalent amount of $Ag[HSO_4]$. The Cd^{II} salt tended to coprecipitate with AgI but at a slower rate. The pure Cd^{II} salt was isolated by evaporating the filtrate after quickly filtering off the initial mixed precipitate. The product was $Cd[HSO_4]_2$·2NCMe.

Reaction of Metals with H_2SO_4 *in* MeCN.—Qualitative experiments showed that Zn, Mg, Bi, Ni, and Cu dissolved quickly in the cold and Tl, Sn, Fe, and Co required heating. Salts were then isolated as follows. Zinc foil was left in a 1% solution of H_2SO_4 in MeCN. The crystals which formed on the foil after 1 h were dried on filter paper and analyzed as $Zn[HSO_4]_2$·4NCMe. They lost MeCN at atmospheric pressure and quickly desolvated to the disolvate *in vacuo*. Nickel foil in 3% acid solution produced a crop of blue crystals within 1 d. After 3 d the liquid was decanted, fresh MeCN added, and the cake of crystals detached. These crystals after quick exposure *in vacuo* analyzed as $Ni[HSO_4]_2$·4NCMe. Manganese and cobalt salts were made similarly. An iron rod reacted only slowly at room temperature but gave sufficient material to identify as a hydrogen sulphate by its i.r. spectrum. On heating under reflux two liquid layers formed. The lower layer crystallized after 3 d. The crystals were dried *in vacuo* for 15 min and analyzed as $Fe[HSO_4]_2$·4.6NCMe. Analytical data are in the Table.

Analytical data (%) for solvated metal hydrogensulphates

	Found			Calc.		
Compound	M	SO_4	H	M	SO_4	H
$Cu[HSO_4]$·4NCMe	19.4	29.5		19.6	29.6	
$Cu[HSO_4]_2$·4NCMe	15.2	45.4		15.1	45.5	
$Zn[HSO_4]_2$·4NCMe	15.1	43.4		15.4	45.4	
$Zn[HSO_4]_2$·2NCMe	18.9	55.3	0.58	19.1	56.2	0.58
$Cd[HSO_4]_2$·2NCMe	28.5	49.5	0.51	28.9	50.0	0.51
$Mn[HSO_4]_2$·2NCMe	16.6	59.1		16.7	58.4	
$Ni[HSO_4]_2$·4NCMe	14.0	46.2	0.47	14.1	46.1	0.48

Reactions of H_2SO_4 with Zn in other solvents were tried since Zn was the most rapidly attacked of the metals. No reactions were observed in dry nitromethane, tetrahydrofuran, or diethyl ether.

Spectral Measurements.—I.r. spectra were measured in solution in MeCN or Nujol mulls: 855w, 895(sh), 910s, 1 010m, 1 055s, 1075(sh), 1 155s, 1 200s, and 1 230m ($Ag[HSO_4]$); 860m, 900(sh), 920s, 1 020m, 1 065s, 1 085m, 1 165m, 1 210s, and 1 240s ($Cd[HSO_4]_2\cdot 2NCMe$); 800w, 847m, 1 055s, 1 065s, 1 173s, 1 245s, and *ca.* 1 350 ($Ag[HSO_4]$ in MeCN) and 852m, 875(sh), 887m, 1 008m, 1 052w(sh), 1 072m, 1 090, 1 100w, 1 175s, 1 260w, 1 292s, and *ca.* 1 340w(sh) cm^{-1} ($K[HSO_4]$).

DISCUSSION

We were unable to prepare $Ag[HSO_4]$ from fused equimolecular mixtures of $Ag_2[SO_4]$ and H_2SO_4. The products always contained both free $Ag_2[SO_4]$ and solvates, as would be expected from the binary phase diagram deduced from the liquidus curve in the $Ag_2[SO_4]$–H_2SO_4 system obtained up to the 1 : 1 composition [2] and the more complete isotherm of the ternary system $Ag_2[SO_4]$–H_2SO_4–H_2O at 25 °C.[9] Silver(I) sulphate is easily distinguished from its 1 and $2H_2SO_4$ solvates, which are present in the binary system, by its insolubility in MeCN. The formation of $Ag_2[SO_4]$ and solvates from the 1 : 1 melt results from an inability to traverse the incongruent m.p. at 126 °C without separation into the solid-phase fields ($Ag_2[SO_4]\cdot H_2SO_4 + Ag_2[SO_4]$) and ($Ag_2[SO_4]\cdot H_2SO_4 + Ag_2[SO_4]\cdot 2H_2SO_4$) above and below the 1 : 1 composition at room temperature. However, pure $Ag[HSO_4]$ was obtained by mixing equivalent amounts of $Ag[O_2CCF_3]$ and H_2SO_4 in CF_3CO_2H under strictly anhydrous conditions. This reaction can be formulated as (5), although this conflicts

$$Ag[O_2CCF_3] + [CF_3C(OH)_2]^+[HSO_4]^- \longrightarrow Ag[HSO_4]\downarrow + 2CF_3CO_2H \quad (5)$$

with a recent report that H_2SO_4 is un-ionized in dry CF_3CO_2H containing the anhydride and indeed that polysulphuric acids form by dehydration.[10] The latter acids have been reported [11] as ionizing in CF_3CO_2H and hence precipitates containing SO_4 : Ag ratios above unity would have been expected. Pure transition-metal salts could not be obtained by this procedure although the proportions of $[HSO_4]^-$ to $[SO_4]^{2-}$ were higher than obtained previously.[4] Possibly irreversible proton transfer occurs from ion pairs such as $[Cu(HSO_4)]^+$ in CF_3CO_2H.

Tetra- and hepta-solvates of $Ag[HSO_4]$ were prepared by contacting an excess of solid $Ag_2[SO_4]$ with H_2SO_4 in MeCN. The heptasolvate, stable below 10 °C, is analogous to those of complex halide salts isolated by Reedijk.[12] The more usual co-ordination is observed in $Ag[HSO_4]\cdot 1.4NCMe$ which is the stable solvate at room temperature. This salt could not be desolvated without reverting to sulphate and acid. The rate of interaction of $Ag_2[SO_4]$ with H_2SO_4 in MeCN solution was more rapid in stirred solutions but was independent of acid concentration at constant $Ag_2[SO_4]$: H_2SO_4 ratio. These results indicate diffusion control through a surface layer.[13] In practical terms the maximum yield in unit time can be obtained in stirred solutions of high acidity.

Solvated salts of transition-metal ions were prepared by metathesis between the silver(I) salt and soluble metal halides or, when the hydrogensulphate was insoluble in MeCN, by growth on metals placed in dilute H_2SO_4 solutions. The latter technique cannot be applied in other aprotic solvents. Thus zinc, the most readily soluble metal in MeCN solutions, is unattacked in nitromethane, tetrahydrofuran, or diethyl ether. These solvated salts could probably be obtained using $[NO][HSO_4]$ to attack metals in MeCN in a similar manner to the previous use of $[NO][BF_4]$ and $[NO][ClO_4]$.[14] Again none of the salts could be desolvated to anhydrous hydrogensulphates. Presumably the temperature required to detach solvent from the cation promotes proton transfer within a hydrogen-bonded anion. Indeed the relative strength of solvent attachment judged by the increase in C–N stretching frequency on co-ordination is $Cd^{II} = Zn^{II} < Cu^{I} < Fe^{III} < Cu^{II} = Ni^{II}$, similar to that observed in complex chlorides [12] and in the same order as the relative resistance to solvent removal ***in vacuo*** at room temperature.

Final attempts to prepare anhydrous hydrogensulphates by controlled hydrolysis of fluorosulphates were unsuccessful and only mixtures of partly hydrolyzed products were isolated.

It is surprising that $Ag[HSO_4]$ is soluble in MeCN but insoluble in aromatic hydrocarbons because silver salts of the strongest acids such as $Ag[ClO_4]$, $Ag[SO_3F]$, and $Ag[MF_n]$ dissolve readily in the latter. A comparison of the i.r. spectra of the new hydrogensulphates based on previous assignments [15-18] suggests that hydrogen bonding is present in the anions in the solid as well as in MeCN solutions, and that the Ag^I ion does not interact appreciably with the anion in $Ag[HSO_4]$ because its spectrum is so similar to that of solvated metal salts. Hence the insolubility of $Ag[HSO_4]$ in hydrocarbons could indicate a failure to disrupt an extended system of hydrogen bonding in the anion, and the solubility in MeCN a disruption to form a small anion unit such as the dimer $[HSO_4H_2SO_4]^-$, also indicated by Kolthoff's acidity measurements which yield a p*K* of -3.6 for $[HSO_4]^- + H_2SO_4 \rightleftharpoons [HSO_4H_2SO_4]^-$ in this solvent.[5]

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[9] E. L. Simons and J. E. Ricci, *J. Amer. Chem. Soc.*, 1946, **68**, 1413.

[10] M. G. Harriss and J. B. Milne, *Canad. J. Chem.*, 1971, **49**, 2937.

[11] J. Bessiere, *Bull. Soc. chim. France*, 1969, 3353.

[12] J. Reedijk, 'Methyl Cyanide as a Ligand,' Thesis, University of Leiden, 1968.

[13] L. L. Bircumshaw and A. C. Riddiford, *Quart. Rev.*, 1952, **6**, 157.

[14] B. J. Hathaway, D. G. Olah, and A. E. Underhill, *J. Chem. Soc.*, 1962, 2444.

[15] G. E. Walrafen and D. M. Dodd, *Trans. Faraday Soc.*, 1961, **57**, 1286.

[16] R. J. Gillespie and E. A. Robinson, *Canad. J. Chem.*, 1962, **40**, 644.

[17] G. E. Walrafen, *J. Chem. Phys.*, 1963, **39**, 1489.

[18] R. Savoie and P. A. Giguère, *J. Chem. Phys.*, 1964, **41**, 2698.