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Behaviour of Some Sulphur–Nitrogen Compounds in Disulphuric Acid

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Abstract

Thiotrithiazyl chloride and thiodithiazyl chloride form $S_4N_3^+$ and $S_3N_2^+$ ions when dissolved in disulphuric acid. Tetrasulphur tetranitride forms S_8^{2+}, $S_2N_2^+$, NH_4^+, SO_2 and NH_2SO_2OH when dissolved in disulphuric acid. From conductance and cryoscopic studies, it is not possible to write an overall stoichiometric reaction for its dissolution.

Several investigations[1–4] have reported the formation of a radical, identified as $S_2N_2^+$, in concentrated sulphuric acid with e.p.r. spectra consisting of five lines which have been identified in terms of hyperfine interactions with two equivalent nitrogen atoms. However, some workers[5,6] have assigned this spectrum to the SN_2^+ radical. Depending upon the ratio of the reactants, tetrasulphur tetranitride forms compounds of composition $S_4N_4,2SO_3$ and $S_4N_4,4SO_3$ with sulphur trioxide[7,8] but, in the presence of excess of sulphur trioxide, these compounds are oxidized to $S_3N_2O_5$ and SO_2. The purpose of the present study is to characterize the stable products of the reaction of some sulphur–nitrogen compounds in disulphuric acid and if possible to establish the stoichiometry of the overall reaction.

Experimental

Tetrasulphur tetranitride, thiotrithiazyl chloride and thiodithiazyl chloride were prepared by the standard methods. The solvent of exact composition was prepared by the method suggested in ref.[9] The conductometric factor γ, the number of moles of $HS_3O_{10}^-$ ions produced per mole of the solute, and the cryoscopic factor ν, the number of moles of ions or neutral species produced per mole of the solute, were obtained by comparison of the conductance and the depression in freezing points of solutions at various concentrations with the calibration curves.[10,11] The amount

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of sulphuric acid formed in a reaction can be found by cryoscopic titrations against sulphur trioxide.[9] Ultraviolet and visible absorption spectra were recorded on a Beckman DB spectrophotometer having quartz cells of path lengths 1 cm to 1 mm.

Results and Discussion

Thiotrithiazyl chloride dissolves readily in disulphuric acid to form clear and stable solutions. No blue solutions due to S_8^{2+} are formed, suggesting that there is no cleavage of the ring. Ultraviolet and visible spectra of the solutions show the presence of a broad band at 240 nm and a small shoulder at 320 nm indicating the presence of the $S_4N_3^+$ cation in the solution.[12] Cryoscopic (ν) and conductance (γ) data support the solvolytic reaction in disulphuric acid as

$$S_4N_3Cl+3H_2S_2O_7 \rightarrow S_4N_3^+ + HSO_3Cl + HS_3O_{10}^- + 2H_2SO_4 \qquad (1)$$

Likewise the solutions of thiodithiazyl chloride are stable and clear in disulphuric acid and the possible solvolytic reaction may be postulated as

$$S_3N_2Cl+3H_2S_2O_7 \rightarrow S_3N_2^+ + HSO_3Cl + HS_3O_{10}^- + 2H_2SO_4 \qquad (2)$$

When tetrasulphur tetranitride was added to disulphuric acid, it formed blue solutions. Ultraviolet and visible spectra of the solutions showed broad bands at 560 and 340 nm attributed to S_8^{2+} ions in the solution.[13,14] A broad band at 290 nm due to sulphur dioxide was also observed, which suggests the formation of sulphur dioxide in the reaction.[15] The amount of sulphur dioxide formed in the reaction increased with time as evidenced by an increase in the optical density of the 290 nm band. The increase in the amount of sulphur dioxide in the solution is partly due to oxidation by the solvent of S_8^{2+} to S_4^{2+} and finally to sulphur dioxide and partly due to the oxidation of the uncharacterized charged species. When these blue solutions were poured onto the crushed ice, only sulphur was obtained, which suggests that there was no protonated species such as $S_4N_4H^+$ or $S_2N_2H^+$ present in the solution. Presence of such species as HCNS or HSNS in 65% oleum has already been ruled out by Jolly and his coworkers.[16] Ultraviolet and visible spectra of the solutions in the present studies show the same intense bands as in 100% sulphuric acid reported by Jolly and his coworkers, suggesting the presence of similar species in the solution. It has now been observed that the rate of solvent oxidation is faster than in the case of sulphuric acid as solvent.

Attempts were made to precipitate the possible cationic species from the solution as a salt by saturating the solution with salts of a suitable anion. Solutions saturated with $KHSO_4$, $K_2S_2O_7$, or $H[B(HSO_4)_4]$ etc. were added to concentrated solutions of tetrasulphur tetranitride in disulphuric acid but in no case did any salt precipitate. Attempts were also made to precipitate the species by lowering the dielectric constant of the solvent by adding thionyl chloride, sulphuryl chloride, or trifluoroacetic acid which are reported to behave as non-electrolytes in disulphuric acid.[9] But up to their limits of solubility, there was no sign of any precipitation.

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Solutions of tetrasulphur tetranitride are not very stable in disulphuric acid. The conductance and the freezing points of the solutions change with time. For each molality the change with time of the conductance and the freezing point of the solution were studied and then extrapolated to zero time. This technique has already been used successfully in the case of solutions of sulphur,[11] selenium[17] and tellurium[18] in disulphuric acid. Conductivity measurements were performed in solutions of S_4N_4 from $0\cdot012$ to $0\cdot138$ mol kg^{-1}. For solutions with concentration range less than $0\cdot03$ mol kg^{-1}, the number of moles of free $HS_3O_{10}^-$ ions in solutions per mole of S_4N_4 added ranged from $1\cdot86$ to $2\cdot00$. At higher concentrations of the solute the relative yield of $HS_3O_{10}^-$ ions decreased markedly. At the highest concentration studied ($0\cdot138$ mol kg^{-1}) the mole ratio was $1\cdot18$; intermediate concentrations showed a consistent trend in the ratio.

It is seen that the ratio $HS_3O_{10}^-/S_4N_4$ is shifted by simple dilution of the solution formed with the solvent. By dilution from $0\cdot138$ to $0\cdot068$ mol kg^{-1}, the $HS_3O_{10}^-/S_4N_4$ ratio changed from $1\cdot32$ to $1\cdot86$. This suggests that the shift in the $HS_3O_{10}^-/S_4N_4$ ratio with change in the concentration of S_4N_4 is due to a shift in some concentration-dependent equilibrium involving $HS_3O_{10}^-$ ions rather than to a change in the stoichiometries of the overall reaction.

Table 1. Values of γ and ν for solutions of sulphur–nitrogen compounds in $H_2S_2O_7$

Compound	At $0\cdot1$ mol kg^{-1}		At $0\cdot15$ mol kg^{-1}		At $0\cdot20$ mol kg^{-1}	
	γ	ν	γ	ν	γ	ν
S_4N_3Cl	1·00	3·0	0·98	2·9	0·97	2·8
S_3N_2Cl	0·98	3·0	0·98	2·9	0·97	2·8
S_4N_4	0·31	2·8	0·32	3·0	0·36	3·5

For some of the solutions, cryoscopic and conductance measurements were performed simultaneously. The data are given in Table 1. As expected, a change in the concentration of S_4N_4 effected a change in the total number of species per mole of S_4N_4 in the same sense as the change in $HS_3O_{10}^-/S_4N_4$ ratio. It is noted that the change in the total number of ions or particles was more than the change in the $HS_3O_{10}^-$ ions. The $HS_3O_{10}^-/S_4N_4$ ratio of about $1\cdot18$ at $0\cdot138$ mol kg^{-1} S_4N_4 is considerably smaller than the corresponding NH_4^+/S_4N_4 ratio of $1\cdot48$. Clearly an additional anion must be present in solution to balance the charge along with the additional positively charged species that might be present.

The limited conductance and cryoscopic data do not permit us to comment on the nature of the reaction of S_4N_4 in disulphuric acid. It may be that, by analogy with sulphuric acid as solvent, the $S_2N_2^+$ cation exists with sulphuric acid and ammonium ions in the solution. We do not have any cryoscopic or conductance data to differentiate between SN_2^+ and $S_2N_2^+$ cations in disulphuric acid.

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