only in strongly acidic media, based on the indicated value for the ionization constant being 0.45. This type of coordination is favored both from statistical and electrostatic considerations. Upon acquisition of a second hydroxylic oxygen following hydrolysis of one fluoride ligand, the coordinating link apparently forms *via* the two acid groups as proposed for PO_3F^{2-}.

Coordination of the metal ion to individual oxygen or fluorine ligands is conceivable for both the $PO_2F_2^-$ and PO_3F^{2-} substrates. This type of interaction is considered less prevalent than chelation as proposed, however. This conclusion arises from the restricted catalytic effect by Th(IV) on the hydrolysis of PO_3F^{2-} and the absence of such an effect by Al(III). In addition, the pH drop observed upon adding Th(IV) to HPO_3F^- suggests that both acid groups participate in the coordination.

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The Reaction of Tetrasulfur Tetranitride with Sulfuric Acid

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The stable products of the reaction of tetrasulfur tetranitride with 100% sulfuric acid are sulfur dioxide, sulfamic acid, bisulfate ion, disulfate ion, ammonium ion, and an unidentified cation which probably contains an S–N bond and which has an intense uv and a complex visible absorption spectrum. The approximate stoichiometry of the overall reaction has been determined by a combination of analytical techniques.

Introduction

The chemistry of tetrasulfur tetranitride (S_4N_4) dates back to 1835, when Gregory[1] obtained the compound by the reaction of disulfur dichloride with ammonia. Since then, many researchers have studied this compound and its large family of derivatives.[2] In this paper, we report the results of our study of the reaction of S_4N_4 with 100% sulfuric acid. Two related studies have been described by other workers.

Goehring and her coworkers[3] have reported the preparation of sulfur trioxide adducts of S_4N_4. Depending on the ratio of reactants, either $S_4N_4 \cdot 2SO_8$ or $S_4N_4 \cdot 4SO_3$ can be formed. When excess sulfur trioxide is used, the sulfur nitride complex is oxidized to $S_3N_2O_5$ and sulfur dioxide is evolved. Subsequent hydrolysis yields more sulfur dioxide as well as ammonia, sulfuric acid, and sulfamic acid. The hydrolysis of S_4N_4 in acidic dioxane–water solutions has been studied by Nair and Murthy.[4] They showed that the principal products are ammonium ion, sulfur dioxide, hydrogen sulfide, and elemental sulfur.

Even before we began our study, it was known that the products of the reaction of S_4N_4 with 100% sulfuric acid were not just a combination of those of the two aforementioned reactions, *i.e.*, the reactions of S_4N_4 with SO_3 and with aqueous acid. Several investigators[5–7] have reported the formation, in freshly prepared "solutions" of S_4N_4 in concentrated sulfuric acid, of a radical which has recently been identified as $S_2N_2^+$. The purpose of this study was to characterize the stable products of the reaction (*i.e.*, those present after the decay of intermediate species such as $S_2N_2^+$) and, if possible, to establish the stoichiometry of the overall reaction.

In order to systematically investigate the reaction, 100% sulfuric acid was used as the solvent instead of ordinary concentrated (95%) sulfuric acid; thus more methods of analysis were applicable. The analytical procedures employed successfully included esr, nmr, electrical conductivity, cryoscopy, uv–visible spectroscopy, and classical chemical analysis.

Experimental Section

General Information.—The 100% sulfuric acid (hereafter designated as H_2SO_4 unless otherwise specified) was prepared by mixing Baker and Adamson reagent grade concentrated H_2SO_4 (95%) and Baker and Adamson reagent grade 15% fuming H_2SO_4. The solution was first adjusted to the point where fuming just stops by the "fair and foggy" method.[8] Exactly 100% acid was obtained by a readjustment with either slightly aqueous or slightly fuming H_2SO_4 until the maximum freezing point was

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attained.[9] The method of determining freezing points is explained in the section on cryoscopy.

The S_4N_4 used was prepared by the method of Villena-Blanco and Jolly[10] and was recrystallized from benzene until the melting point reached 186°. The product was then stored under vacuum until needed.

The reactions of S_4N_4 with H_2SO_4 usually were studied on a standard vacuum line. The H_2SO_4 was first degassed, and the S_4N_4 was slowly added from a tipping side arm. In order to prevent local heating by the exothermic reaction, the solution was stirred magnetically and kept in an ice bath as long as there was evidence of reaction. In general, physical measurements were made using solutions which had been kept for several days and which contained a negligible concentration of radical species.

Conductivity.—It has been shown by Gillespie and Wasif[11] that very accurate determinations of bisulfate ion concentrations in H_2SO_4 can be achieved by conductivity measurements. The mobility of bisulfate ion is so much higher than that of any other species in H_2SO_4 that the conductance can be considered to be a measure of just that ion's concentration.[12]

The conductivity cell was of the basic design of Gillespie.[13] The solutions were maintained under an atmosphere of dry nitrogen, and the cell was placed in a bath thermostated at 25 ± 0.005°. The measurements were made with an ac Wheatstone Bridge using a 1000-cps oscillator as the signal source and a Tektronix Type 532 oscilloscope as the balance point detector. A balance point to better than 1 ohm in 2500 ohms could be obtained.

The cell was calibrated with reagent grade ammonium sulfate. A plot of ammonium sulfate concentration *vs.* conductivity was drawn. The data of different runs were found to be consistent to better than 0.2%. The concentrations of bisulfate ion in the S_4N_4 "solutions" used in this study were determined by measuring the conductivity of the solution and by reading the bisulfate ion concentration from the plot.

Cryoscopy.—The freezing point depression method has been shown by Gillespie, *et al.*,[14] to be an accurate method for determining the total concentration of all species in H_2SO_4 solutions. The cryoscopic constant for H_2SO_4 has been shown to be 6.12 kg deg mol^{-1} and the freezing point to be 10.371°. The measurements were performed in a closed system with an atmosphere of dry nitrogen kept over the solution. The temperature was measured with a Hewlett-Packard quartz thermometer placed in a mercury-filled glass well to ensure good thermal contact. Stirring was accomplished by the up and down motion of a glass spiral attached to a glass-enclosed iron rod. The stirring motion was effected by a periodically actuated magnetic solenoid surrounding the upper tube.

The solution was cooled below the freezing point with a cold water bath, and the supercooled solution was seeded by touching the outside with a liquid nitrogen cooled swab. An air jacket was placed around the outer tube, which was submerged in a cold bath and allowed to warm. Every 17 sec the temperature was automatically printed out on a Hewlett-Packard digital printer. All readings were recorded to 0.0001°. The temperature was then plotted against time, and the melting point was determined as the intercept of the two straight segments of the curve. These segments corresponded to the temperature regions in which the solution was in contact with solid H_2SO_4 and in which the sample was completely melted.

The freezing point of the pure sulfuric acid was found to be 10.409 ± 0.002°. The quartz thermometer was very accurate for determining temperature differences over a small range, but it was not as precise for determining true temperatures. Therefore, the freezing point used to calculate the freezing point depression was the one determined in this study rather than the reported value of 10.371°.

The total number of species in solution was calculated using the formula[14]

$$\nu = \theta(1 + 0.002\theta)/(6.12m_s) - m_d/m_s$$

where ν is the total moles of species in solution per mole of solute, θ is the freezing point depression (from the ideal undissociated value which is 0.245° higher than the actual freezing point of pure H_2SO_4), m_s is the stoichiometric concentration of solute in moles per kilogram of solvent, and m_d is the total concentration of self-dissociation species (H_2O, H_3O^+, H^+, $H_2S_2O_7$). m_d values were determined from the tables of Bass, Gillespie, and Robinson[14] from the known concentration of HSO_4^- in the solution.

Nmr.—A Varian A-60 spectrometer was used. Signal intensities were measured using $[Co(NH_3)_6]_2[SO_4]_3$ (which is soluble in H_2SO_4 and which gives one moderately sharp peak) as an internal standard. The $[Co(NH_3)_6]_2[SO_4]_3$ was itself compared with purified $(NH_4)_2SO_4$ as a check on the accuracy of the method. The results consistently showed less than 2% error.

Uv–Visible Spectra.—The uv and visible spectra were obtained with a Cary 14 spectrophotometer, using quartz cells. Various path lengths, from 0.1 mm to 5 cm, were used in order to obtain reasonable absorbances in each spectral region.

Ionic Polarity.—To determine the sign of the charge on the species with the intense uv band, an electrolysis cell, containing five compartments separated by medium-porosity glass frits, was used. Solvent was placed in the four outer compartments, and the solution being studied was placed in the center. A dc potential of 15 V was applied across the cell for several hours, during which time the cell was kept in a cold water bath to prevent decomposition of the solution. By examining the spectra of the solutions from the three central compartments, the direction in which the species preferentially migrated (and consequently its polarity) was determined.

Results

General Information.—When S_4N_4 and H_2SO_4 were mixed under vacuum, the evolution of sulfur dioxide (identified by ir and mass spectrometry) began immediately. When the solution was kept at room temperature or below, the sulfur dioxide was evolved slowly, and, after a few hours or a few days (depending on the concentration of S_4N_4), the amount of sulfur dioxide evolved invariably leveled off at 2.00 ± 0.02 mol per mole of S_4N_4. The final ratio was the same regardless of the concentration, as long as there was sufficient H_2SO_4 to react with all the S_4N_4.

When a sample of S_4N_4 enriched in ^{33}S to the extent of 48.6% was treated with sulfuric acid, mass spectrometric analysis of the resulting sulfur dioxide showed that it came completely from the S_4N_4. (The sulfur ratios were determined on a CEC Model 21-620 mass spectrometer, and the results showed no deviation between the $^{33}S/^{32}S$ ratio in the S_4N_4 and in the resulting sulfur dioxide.)

In fairly concentrated "solutions" (above 0.01 *m*[15]) of S_4N_4 a fine precipitate formed. The precipitate was isolated and shown to be sulfamic acid, NH_3SO_3, on the basis of a mixture melting point and comparison of the ir spectrum with that of a commercial sample of NH_3SO_3. The total amount of sulfamic acid precipitated was determined by Kjeldahl analysis for four "solutions" which were approximately 0.15 *m* in S_4N_4. The data, after correcting for a small amount of dissolved

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(13) R. J. Gillespie, J. V. Oubridge, and C. Solomons, *ibid.*, 1804 (1957).
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(15) Most concentrations in this paper are expressed as molality (moles per kilogram of solvent), abbreviated as *m*.

sulfamic acid, showed that 1.49 ± 0.02 mol of NH_3SO_3 formed per mole of S_4N_4. A small amount of elemental sulfur was always produced in these concentrated "solutions." It had no appreciable solubility in sulfuric acid and was collected with the sulfamic acid precipitate. Water washings removed all the sulfamic acid; the weighed residue corresponded to approximately 0.1 mol of sulfur per mole of S_4N_4.

Nmr.—The nmr spectrum of the solution left after filtering off the sulfamic acid consisted of a triplet (6.3 ppm downfield from TMS) with a 53-cycle splitting corresponding to ammonium ion. When the spectrum was taken shortly after the reaction had begun, the triplet was very broad. The broadening was due to the paramagnetic species $S_2N_2^+$ in solution. As this radical decomposed, the nmr lines sharpened until they had a width at half-height of approximately 4 cps, which is almost as sharp as the lines of an ammonium salt dissolved in pure sulfuric acid.

The nmr-determined yields of ammonium ion, expressed as moles of NH_4^+ per mole of S_4N_4 consumed, are listed as found for solutions having the *nominal* S_4N_4 molalities indicated in parentheses: 1.20 (0.143), 1.32 (0.151), 1.56 (0.153), 1.45 (0.159), 1.50 (0.170), 1.43 (0.333). There appears to be no trend in the data, and the wide variations in the results cannot be attributed to experimental error, which is approximately ±5%. We believe that the observed variation in the results can be attributed to a general nonreproducibility of the reaction stoichiometry. Probably two or more decomposition reactions take place simultaneously, and variations in the rate of each reaction cause measurable shifts in the overall stoichiometry.

Conductivity and Cryoscopy.—Conductivity measurements were performed on solutions of nominal S_4N_4 concentrations ranging from 0.012 to 0.16 *m*. For solutions less than 0.02 *m* the number of moles of free HSO_4^- in solution per mole of S_4N_4 added ranged from 0.94 to 1.00. Upon going to higher concentrations the relative yield of HSO_4^- decreased quite markedly. At the highest concentration studied (0.153 *m*), the mole ratio was 0.53, with intermediate concentrations showing a consistent trend in the ratio.

It was shown that the HSO_4^-/S_4N_4 ratios could be shifted by simply diluting the solution, once formed, with sulfuric acid. For example, by dilution from 0.151 to 0.036 *m*, the HSO_4^-/S_4N_4 ratio was shifted from 0.527 to 0.916. These data indicate that the shift in the HSO_4^-/S_4N_4 ratio with change in the nominal S_4N_4 concentration is due to a shift in some concentration-dependent equilibrium involving bisulfate ion, rather than to a change in the stoichiometry of the overall reaction.

For some of the solutions, cryoscopic and conductivity measurements were performed simultaneously. The data are presented in Table I. As might be expected, changes in the nominal S_4N_4 concentration affected the total number of species per S_4N_4 in qualitatively the same way as they affected the HSO_4^-/S_4N_4 ratio. It should be noted, however, that the changes in the total species were much greater than the changes in the bisulfate ion.

TABLE I

CONDUCTIVITY AND CRYOSCOPY RESULTS

Nominal S_4N_4 concn, *m*	HSO_4^-/S_4N_4	Total no. of species per S_4N_4	Nominal S_4N_4 concn, *m*	HSO_4^-/S_4N_4	Total no. of species per S_4N_4
0.1530	0.529	4.38	0.0501	0.744	4.94
0.1512	0.527	4.33	0.0482	0.782	4.85
0.1434	0.533	4.38	0.0260	0.916	5.10
0.0519	0.738	4.97	0.0257	0.870	5.20

The HSO_4^-/S_4N_4 ratio of about 0.5 at nominal S_4N_4 concentrations around 0.15 *m* is considerably smaller than the corresponding NH_4^+/S_4N_4 ratio of approximately 1.4. Clearly an additional anion must be present in solution to balance the charge of the ammonium ion, not to mention any additional positively charged species that might be present. This anion must be the conjugate base of an acid as strong as, if not stronger than, H_2SO_4. The most likely candidate, noting the stoichiometric restrictions, is $HS_2O_7^-$, the conjugate base of disulfuric acid ($H_2S_2O_7$). The $HS_2O_7^-$ ion is known to react with water as in

$$HS_2O_7^- + H_2O \rightleftharpoons H_2SO_4 + HSO_4^-$$

In order to obtain evidence for the $HS_2O_7^-$ ion, we measured the changes in the melting point of S_4N_4 solutions as water (in the form of concentrated H_2SO_4) was incrementally added. We found that the melting point of the solutions initially rose rather sharply, leveled off, and then decreased upon further addition of water. A plot of melting point *vs.* added water for one of these "titrations" is shown in Figure 1. The shape of the curve can be explained by the presence of disulfuric acid ($H_2S_2O_7$) in equilibrium with its conjugate base according to[14]

$$H_2S_2O_7 \rightleftharpoons H^+ + HS_2O_7^- \qquad (1)$$

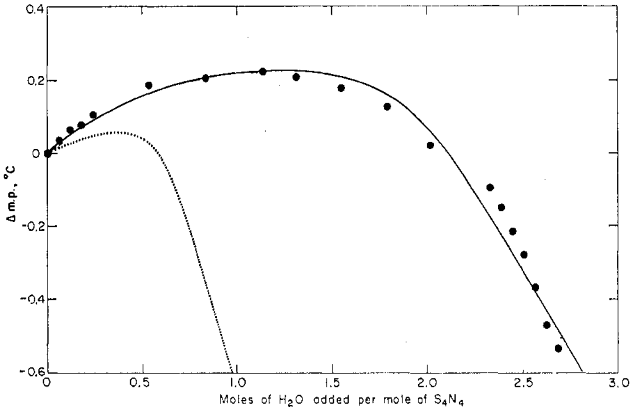

Figure 1.—Cryoscopic "titration" of 0.15 *m* S_4N_4 in H_2SO_4 with water (added as concentrated H_2SO_4). See text for significance of curves.

The initial rise in the melting point upon adding water presumably was due to a decrease in solute species as disulfuric acid and water reacted to form solvent sulfuric acid. However, any attempt to predict quantitatively the curve of Figure 1 must account for the additional equilibria

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- \quad (2)$$

$$2H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^- \quad (3)$$

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \quad (4)$$

From the equilibrium constants for reactions 1–4 and from measured values of the HSO_4^- concentration at two different dilutions, it was possible to calculate the concentrations of all the species in these reactions. It was then possible to calculate the net change in the concentration of each of these species upon subsequent additions of water and thus to calculate a theoretical titration curve.

The dotted curve in Figure 1 was calculated using the equilibrium constant values of Gillespie and Robinson[16] (K_1 = 1.4 × 10^{-2} mol/kg, K_2 = 1 mol/kg, K_3 = 3.5 × 10^{-5} mol^2/kg^2, K_4 = 1.7 × 10^{-4} mol^2/kg^2). Obviously these constants give a very poor fit to the experimental points. Also, the calculated value of the disulfate ion yield is too low to maintain charge neutrality. (The calculated species yields are $HS_2O_7^-/S_4N_4$ = 0.494, $H_2S_2O_7/S_4H_4$ = 0.080, and HSO_4^-/S_4N_4 = 0.491.)

In view of the complexity of the solutions and their high ionic strength, it is reasonable to assume that the applicable equilibrium constants for reactions 1–4 would be considerably different from those reported by Gillespie, *et al.* By adjusting the values of these constants, it was possible to obtain the good fit shown by the solid curve in Figure 1. This curve corresponds to the following constants and yields K_1 = 3 × 10^{-3} mol/kg, K_2 = 4 × 10^{-3} mol/kg, K_3 = 1 × 10^{-5} mol^2/kg^2, K_4 = 3.5 × 10^{-5} mol^2/kg^2, $HS_2O_7^-/S_4N_4$ = 1.60, $H_2S_2O_7/S_4N_4$ = 0.30, and HSO_4^-/S_4N_4 = 0.40. It is disturbing that the adjusted value of K_2 is of an entirely different order of magnitude from that of Gillespie, *et al.* However, we shall accept the latter yields, with the realization that they are *very* uncertain.

When making the preceding calculations, we assumed the absence of ion pairing. To test the validity of this assumption, we determined the melting point of a 0.25 *m* ammonium sulfate solution in sulfuric acid (0.50 *m* ammonium bisulfate). The result corresponded to 3.99 mol of species per mole of ammonium sulfate. Thus, to the precision of the technique employed, there was no ion pairing by the ammonium and bisulfate ions.

Uv–Visible Spectroscopy.—The analyses for sulfamic acid (1.49 NH_3SO_3/S_4N_4) and for ammonium ion (1.2–1.6 NH_4^+/S_4N_4) account for 2.7–3.1 nitrogen atoms per S_4N_4. Thus 0.9–1.3 nitrogen atoms per S_4N_4 are unaccounted for and are presumably present in the form of one or more as yet unidentified species. In the hope of obtaining information about such species, optical spectroscopic investigations were initiated.

Immediately after mixing S_4N_4 with sulfuric acid, a rather complex spectrum is observed: a broad peak at 4560 Å, a multiplet centered around 4000 Å, an intense absorption at 3260 Å, and an extremely intense absorption at 2140 Å. The peaks at 4560 Å and 3260 Å decay rapidly according to first-order rate laws with half-lives of 22 and 40 min, respectively. As the peak at 3260 Å decays, a shoulder at 3510 Å becomes apparent, and then the latter peak decays by first-order kinetics with a half-life of 48 hr. These absorptions always show first-order decay; however, the half-times vary with the reaction condition. When the sample is not continuously evacuated to remove all evolved sulfur dioxide, the half-lives are those reported. However, when evacuated, the bands decay much more rapidly.

The effect of sulfur dioxide in the reactions has not been investigated, and the exact nature of the species corresponding to the transient absorption bands has not been determined. The spectrum remaining after 4 days of pumping on a sample is shown in the upper part of Figure 2. The multiplet in the visible region and the single peak in the uv region always appear together in the same intensity ratio and show no further change on standing. Assuming that the absorptions correspond to one species per S_4N_4 the maximum extinction coefficients in the visible and uv regions are 58 and 27,000 M^{-1} cm^{-1}, respectively.

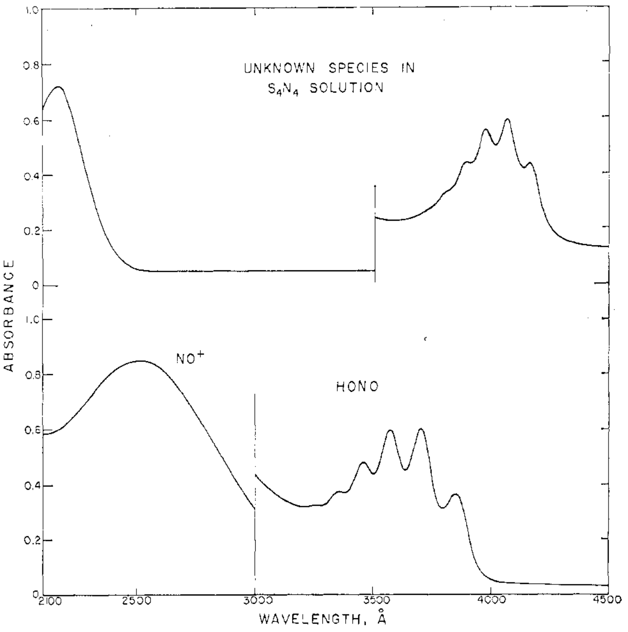

Figure 2.—Uv and visible spectra of H_2SO_4 solutions: top, 0.002 *M* S_4N_4 in 100% H_2SO_4 (uv spectrum taken in 0.013-cm cell; visible spectrum taken in 5.00-cm cell); bottom, 0.004 *M* $NaNO_2$ in H_2SO_4 (uv spectrum taken in 0.050-cm cell in 71% H_2SO_4; visible spectrum taken in 5.00-cm cell in 44% H_2SO_4).

The stable spectrum apparently does not correspond to any known species. Indeed, the splitting of the visible band is quite unexpected in such a highly polar and highly hydrogen-bonding solvent as sulfuric acid. Generally the greater orientation of solvent molecules in highly polar solvents tends to obscure vibrational fine structure.[17] However, the spectrum of nitrous acid in

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[16] R. J. Gillespie and E. A. Robinson, "Non Aqueous Solvent Systems," T. Waddington, Ed., Academic Press, London, 1965.

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aqueous sulfuric acid, shown in the lower part of Figure 2, shows some resemblances. The multiplet and the intense singlet have been assigned to HONO and NO^+, respectively. By adjusting the sulfuric acid concentration, the relative concentrations of these two species can be altered by shifting the equilibrium.[18]

$$HONO + H^+ \rightleftharpoons NO^+ + H_2O$$

At sulfuric acid concentrations above 70%, essentially all of the nitrous acid is converted to NO^+. The splitting between the two lowest energy peaks of the HONO spectrum is 1015 cm^{-1} —a frequency which is close to the vibrational frequency of free NO, *i.e.*, 958 cm^{-1}.[19] The splitting between the two lowest energy peaks in the solution under study is 580 cm^{-1}. This corresponds rather closely to the vibration frequency of free NS, *i.e.*, 610 cm^{-1}.[20] This analogy suggests that the species under study contains an NS terminal group.

If the spectrum is due to sulfur analogs of HONO and NO^+, such as HONS and NS^+, the latter species would be expected to shift their relative concentrations upon changing the sulfuric acid concentration. When the sulfuric acid strength was varied from 95% sulfuric acid to 15% fuming sulfuric acid there was only a 5% shift in the relative absorptions. Over this range both the water activity and hydrogen ion activity change by several orders of magnitude,[21] and the relative intensities would be expected to reflect this change. The small observed shift probably was caused by a change in the extinction coefficient on altering the properties of the solvent.

When a 20-fold excess of ammonium sulfate was added to the solution in 100% sulfuric acid, the ratio of the two absorptions changed only by a few per cent. This result again could be accounted for by a change in the nature of the solvent.

Upon adjusting the temperature of the cell compartment from 5 to 40°, a change in the peak intensities would be observed if the visible and uv peaks were due to two species in equilibrium and if they had a nonzero heat of conversion. We found essentially no shift in the relative peak heights over this temperature range. Thus, the two absorptions at 2140 and 4000 Å appear to be due to a single species in solution.

In order to permit comparison of the spectrum with that of a compound known to have a terminal SN group, the gas-phase electronic spectrum of NSCl was obtained. Solid $S_3N_3Cl_3$ exists in equilibrium with the gaseous monomer NSCl. $S_3N_3Cl_3$ was prepared according to the method of Schröder and Glemser[22] by the reaction of Cl_2 with S_4N_4. The product was recrystallized twice from CCl_4 and gave a sharp melting point at 89° (lit. mp 91°,[23] 98°[24]). A sample was transferred to a 2-cm quartz absorption cell equipped with a ball joint. The cell was attached to a standard vacuum line, evacuated, and then sealed off. At room temperature (23°) the vapor spectrum consisted of only one very strong peak at 2140 Å. The intensity of the absorption increased with time until the equilibrium vapor pressure was reached, at which time the peak was well off scale on the Cary 14 spectrophotometer. At 5° the peak absorbance stabilized at 2.33, and its extinction coefficient was calculated (using Patton and Jolly's vapor pressure data[24]) to be 11,300. As the temperature was raised, many sharp, weak absorptions appeared in the range 3600–4900 Å. At 60° at least 59 distinct absorptions with recurrent splittings could be seen.

A gas-phase sample might be expected to show many more vibrational splittings than a species in solution.[17] The fact that the unknown sulfuric acid solution and NSCl vapor both have an intense absorption peak at the same wavelength in the uv region and a complex multiplet in the visible region supports the idea that the unknown species in sulfuric acid contains an SN terminal group.

Ionic Polarity.—A solution of S_4N_4 in sulfuric acid was placed in the central compartment of a five-compartment transference cell for a determination of the polarity of the species exhibiting the spectrum of Figure 2. A 15-V dc potential was applied for 2 hr with the cell in a 10° bath. The solutions from each compartment were then examined by uv–visible spectroscopy. The species was found to migrate to the cathode (negative electrode), and the relative intensities of the absorption remained the same. This result established that the species is positively charged.

Isolation Attempts.—Attempts were made to precipitate the cationic species as a salt by saturating the solution with salts of suitable anions. Solutions saturated with salts of HSO_4^-, $HS_2O_7^-$, and $B(HSO_4)_4^-$ were added to concentrated S_4N_4 solutions, but in no case was any salt precipitated.

Attempts were made to precipitate the species by lowering the dielectric strength of the solvent. Sulfuryl chloride ($SOCl_2$) and nitromethane (CH_3NO_2) are both nonelectrolytes, but up to their solubility limits there was no sign of precipitation.

Discussion

The analytical data can be summarized in the form of the following equation for the net reaction of S_4N_4 with sulfuric acid

$$S_4N_4 + 6.8H_2SO_4 \longrightarrow 2.0SO_2 + 1.5NH_3SO_3 + 1.5NH_4^+ + 0.1S + {\sim}1.6HS_2O_7^- + {\sim}0.4HSO_4^- + {\sim}0.3H_2S_2O_7 + [0.5S_6N_2O_8H^+]$$

It should be emphasized that the coefficients for $HS_2O_7^-$, HSO_4^-, and $H_2S_2O_7$ are very inaccurately known. The last species in the equation was empirically formulated to balance the atoms and charges. In view of the uncertainties in the analytical data, particularly in the yields of $HS_2O_7^-$, HSO_4^-, and $H_2S_2O_7$, the formula of this species has practically no significance. We do

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[19] G. Herzberg, "Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand Co., Inc., Princeton, N. J., 1966.

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know that an unidentified cationic species, probably containing at least one SN linkage, is formed in high yield. (If less than 0.5 mol of this species forms per mole of S_4N_4, its uv molar extinction coefficient exceeds 54,000 M^{-1}—a value which is unusually high.) Clearly the reaction of S_4N_4 with sulfuric acid cannot be said to be understood until this important species is identified.

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Intramolecular Environmental Effects on the Bonding of Cyanide and Carbonyl

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The bonding characteristics of carbon monoxide and cyanide ion in transition metal complexes are examined *via* molecular orbital calculations on the isoelectronic series of complexes Mn(CO)$_6^+$, Mn(CO)$_5$CN, Mn(CN)$_5$CO^{4-}, and Mn(CN)$_6^{5-}$. Within the series, it is found that trends in carbonyl bonding can be attributed essentially to variations in π-acceptor ability. On the other hand, the bonding of cyanide appears to be a function of both σ-donor and π-acceptor abilities which vary according to the total intramolecular environment. Contrary to mixed systems of π donors and π acceptors, such as Mn(CO)$_5$Cl, the present complexes do not exhibit electron distributions which would predict significant trans influence. As the ligands are varied in the series, the metal atom acts primarily as a transmitter of electron density among the changing ligand systems.

I. Introduction

In our recent studies on the bonding in hexacarbonyl[2] and pentacarbonyl halide[3] complexes, we were intrigued by the observation that the trends in bonding characteristics of the CO group could be described by the changes in the antibonding π-orbital occupations only. Based upon the reasonable assumption that all 1s electrons were in the core, our calculations showed that the orbital occupations $(1\sigma)^2(2\sigma)^2(1\pi)^4(3\sigma)^{1.35}$ remained essentially constant. Thus, except for the loss of 0.65 electron per ligand *via* σ bonding, the only noticeable changes were in the occupations of the 2π orbitals. A similar observation held for the nitrosyl groups in a series of metal pentacyanonitrosyl complexes.[4] If this situation is general, it would permit calculational simplifications, such as a decrease in the size of the basis set. In addition, qualitative bonding discussions of π acceptors in which only changes in π occupation were considered would be on a firm footing. However, certain factors suggested that it would be unwise to generalize the observed constancy of σ-orbital occupation. For example, it appears that variation in σ-bond strength is required to interpret the trends in CN force constants in systems not involving metal complexes.[5] Furthermore, our experience with the halogen energy levels in the manganese pentacarbonyl halides[3] indicated that the halogen σ- and π-donating ability was drastically different than what one might expect from their bonding in hexahalide complexes. This latter experience led us to compare the σ-donor–π-acceptor abilities of cyanide and carbonyl relative to one another within the four complexes Mn(CO)$_6^+$, Mn(CN)$_6^{5-}$, Mn(CO)$_5$CN, and Mn(CN)$_5$CO^{4-}.

There were several reasons for our choices of the complexes to be studied. The systems are isoelectronic and closed shell. Of the four complexes, only Mn(CN)$_5$CO^{4-} has yet to be prepared so that useful experimental information such as infrared stretching frequencies are available. In the first two complexes, the ligands compete only with themselves for the metal d_π electrons while in the latter two a single CN ligand is in the presence of five CO ligands and *vice versa*. These extremes permit examination of relative σ-donor and π-acceptor abilities as a function of the total ligand environment. Finally, since the complexes include a cation, anions, and a neutral molecule, one might expect to observe substantial changes in metal orbital occupations and relative positions of the eigenvalues.

II. Procedure

The computations used here are identical with those used in our previous work on the pentacarbonyl halides.[3] As was the case in the pentacarbonyl halide calculations, the unique ligand, B, in MA_5B systems was presumed to be located along the positive z axis. The computational approximations are rotationally invariant and this choice is for convenience only. The internuclear distances were chosen as follows.

For all the complexes, the intraligand distances for CO and CN$^-$ were set at 1.128 Å[6] and 1.160 Å,[7] re-

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