erable evidence in the literature on the formation of complexes between alkyl halides and Friedel-Crafts catalysts from measurements of conductivity,[10,11] dielectric polarization,[12] vapor pressures,[13] and spectra,[14] and solid complexes of $GaCl_3$ and $AlBr_3$ with methyl halides have been isolated.[13] The kinetics for the propylation of benzene with $GaCl_3$ in CS_2 solution can be interpreted in terms of a complex between $GaCl_3$ and propyl chloride which is almost as stable as that between $GaCl_3$ and benzene.[15] On the basis of these other studies, and the fact that where they have been determined[13,14] the heats of formation of these complexes are quite small, it is at least not unreasonable to postulate a fairly stable complex between $SnCl_4$ and 2-chlorobutane even at 160°.

An extrapolation of the data to 200° gives a value of about 10^{-4} sec.$^{-1}$ for k_1. This can also be expressed in terms of a second-order rate constant using the concentrations of uncomplexed $SnCl_4$ and 2-chlorobutane, *i.e.*, $k_2 = k_1/K = 10^{-3}$ l.-moles^{-1} sec.$^{-1}$ where $R = k_2(SnCl_4)(C_4H_9Cl)$. The previous data on the lack of exchange between $SnCl_4$ and 2-chlorobutane in the vapor phase in 180 minutes at 200°[1] are only accurate enough to show that the second order rate constant is less than 2×10^{-3} l. moles^{-1} sec.$^{-1}$. Thus, although it is unlikely on other grounds, the available data do not exclude the possibility of a homogeneous vapor phase exchange between $SnCl_4$ and 2-chlorobutane at elevated temperatures with a rate constant of the same order of magnitude as that in heptane solution.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Disulfur Monoxide. I. Its Identification as the Major Constituent in Schenk's "Sulfur Monoxide"

BY DAVID J. MESCHI AND ROLLIE J. MYERS

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The product of an electric discharge through sulfur and SO_2 has been reported by several workers to be a mixture of SO and S_2O_2 in the gas phase. On the basis of mass spectrographic, stoichiometric and gas effusiometric measurements it is shown that this material is a mixture of SO_2 and disulfur monoxide, S_2O. The presence of any S_2O_2 in this product is highly improbable, though it is possible that a small amount of SO may be present in the mixture. The properties previously attributed to the presence of SO or S_2O_2 in the discharge product are shown to be due to S_2O.

In a series of papers Schenk[1] discussed the preparation and properties of a lower oxide of sulfur which he characterized as "sulfur monoxide." This new oxide can be prepared in purest form by passing a high voltage discharge through a mixture of sulfur vapor and SO_2 at a total pressure of a few mm. of mercury. Schenk also reported that his "sulfur monoxide" could be identified as a product from the combustion of sulfur at low oxygen pressures, the thermal decomposition of $SOCl_2$ and $SOBr_2$ and from their reaction with certain metals. The gaseous "sulfur monoxide" is stable in a clean glass system for several hours at a pressure of a few mm. of mercury, but it decomposes rapidly at pressures greater than 30 mm. When this lower oxide is condensed in a low temperature trap an orange-red solid is obtained. This solid decomposes into sulfur and SO_2 when warmed to room temperature.

Schenk initially characterized this oxide as sulfur monoxide from the fact that it has an intense ultraviolet absorption spectrum in the same region as the well established emission spectrum of SO. In addition Schenk found that what he believed to be the pure oxide had a sulfur to oxygen ratio of 1:1. Kondrat'eva and Kondrat'ev[2] present stoichiometric evidence that the formula of Schenk's "sulfur monoxide" is S_2O_2. In addition they show that the ultraviolet absorption spectrum of "sulfur monoxide" does not correspond to the SO emission spectrum. Jones[3] re-examined the ultraviolet spectrum under high resolution and concluded that "sulfur monoxide" was probably S_2O_2 with a structure similar to that of SO_3.

During an investigation of the microwave spectrum it became clear that neither SO or S_2O_2 could fit the observed spectrum. The stoichiometry of "sulfur monoxide" also became uncertain in light of the work of Rao.[4] While investigating the properties of "sulfur monoxide," Rao observed that when the low pressure combustion products of sulfur were passed through CCl_4 a deep yellow colored solution resulted. When the CCl_4 solution was purified by a stream of oxygen Rao found that the

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[1] First paper, P. W. Schenk, *Z. anorg. allgem. Chem.*, **211**, 150 (1933); for a review see P. W. Schenk, *Chem. Z.*, **67**, 273 (1943) or E. Maxted, "Modern Advances in Inorganic Chemistry," Oxford, 1947.

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dissolved material had a formula corresponding to disulfur monoxide, $(S_2O)_x$. Murthy[5] also showed that if Schenk's "sulfur monoxide" is condensed in a trap and warmed to −30°, the residue has a sulfur to oxygen ratio of 2:1.

In this paper we show that Schenk's "sulfur monoxide" is in the gas phase a mixture of SO_2 and S_2O. In addition, all of the properties previously attributed to sulfur monoxide in Schenk's product are due to the presence of S_2O. Since Schenk's "sulfur monoxide" is in reality disulfur monoxide, S_2O, we shall hereafter use this latter name.

Experimental Methods[6]

Generator.—The disulfur monoxide was prepared by passing a 60 c.p.s. discharge through a mixture of SO_2 and sulfur vapor. The discharge tube was similar to that used by Jones.[3] For the majority of the work the SO_2 was supplied at a pressure of 0.1–0.3 mm. of mercury. The best operating conditions at these pressures were found when the sulfur supply was near 130° and the discharge tube near 150°.

Mass Spectrum.—The mass spectra were taken at the Emeryville Laboratories of the Shell Development Company. The instrument utilized had an inlet system volume of 2 l. which was all glass except for a metal stopcock, a Pirani gage wire and a gold thimble inlet to the mass spectrograph. The disulfur monoxide samples were stored in the inlet system for periods ranging from less than 5 min. to nearly 20 min. It was observed that the mass 80 peak was strongest for the shortest period of storage in this inlet system. The samples used for mass spectrographic analysis were prepared one hour previous to their use. They were stored in 1-l. glass bulbs at a pressure of 0.2 to 0.3 mm. The ionizing electrons in the mass spectrograph were accelerated to a potential of about 75 volts.

Stoichiometry.—The SO_2 content of the disulfur monoxide samples was determined by ultraviolet absorption. In the region near 3,000 Å. the SO_2 absorption is masked by the stronger S_2O system, but near 2,100 Å. there is a strong SO_2 system which is free of S_2O absorption. Using a 10 cm. gas cell and a Beckman DU spectrophotometer, we found that it was possible to measure the SO_2 content in the range 0–0.2 mm. to better than 0.002 mm.

The optical densities of a band maximum near 2078 Å. and the minimum 9 Å. lower were both measured. The difference between these two readings was plotted against pressure and a curve of growth for SO_2 was constructed using pure SO_2. The instrument was operated at constant slit width to give an effective band width of 8 Å. The partial pressure of the SO_2 in the disulfur monoxide samples was determined using this curve of growth.

The total pressure of the disulfur monoxide samples was determined utilizing a Western Electric Thermistor, type D176980, as a Pirani gage. The thermistor element is 0.013 inches in diameter and encased in glass. The four 0.001 inch diameter supporting wires were allowed to contact the gas, but the larger copper supporting wires were coated with Glyptal. The thermistor was operated in a bridge circuit at a temperature of about 60°. This Pirani gage was calibrated with SO_2 and the calibration was used for both SO_2 and S_2O.

The decomposition of S_2O into sulfur and SO_2 was accomplished by freezing the sample down in a trap following the method of Schenk.[1] The resulting condensate was alternately heated by a flame and cooled with liquid N_2 until the room temperature pressure was constant. Three heatings and coolings usually were sufficient.

Molecular Weight Determination.—The gaseous effusion apparatus was similar to that of Harris and Nash.[7] For disulfur monoxide, however, it was found necessary to use an apparatus with a single carefully greased stopcock, to use a bulb volume of 500 ml. and to make effusion measurements at pressures below 0.01 mm. The half-time of the effusiometer was about 5 min. During a run of 15 min. duration experiments indicated that decomposition of S_2O in the effusiometer amounted to considerably less than 1%. The pressure in the effusiometer bulb was measured utilizing the previously described thermistor Pirani gage. The half-time of the effusiometer was determined for SO_2 immediately before an S_2O determination. In order to minimize decomposition, the samples were taken directly from the generator to the effusiometer bulb and an entire effusiometer run, 0.01 to 0.001 mm., was displayed by a Brown recording potentiometer while at the same time an ultraviolet analysis for the SO_2 content was being done on the sample.

Experimental Results

The mass spectra of disulfur monoxide samples were run in order to determine the relative importance of S_2O_2 and S_2O. It was quickly observed that there was no mass peak corresponding to $S_2O_2^+$ but there was a prominent one corresponding to S_2O^+. A list of relative peak intensities is given in Table I.

TABLE I

MASS SPECTRUM OF A DISULFUR MONOXIDE SAMPLE

Ion	Mass no.	Relative peak heights[a] Sample 2a	2b[b]
SO^+	48	9.25	9.25
SO^+	49	0.10	0.08
SO^+	50	0.43	0.43
OCS^+	60	0.23	0.22
SO_2^+	64	25.60	26.20
SO_2^+	65	0.22	0.23
SO_2^+	66	1.26	1.29
CS_2^+	76	5.66	5.56
CS_2^+	77	0.14	0.15
CS_2^+	78	0.50	0.50
S_2O^+	80	7.73	5.10
S_2O^+	81	0.12	0.09
S_2O^+	82	0.71	0.47

[a] For the mass range 48–150. [b] Sample 2b was stored in the mass spectrograph inlet system for approximately 10 min. longer than 2a.

It can be seen from Table I that the mass 80 peak is subject to rapid decay when the sample is stored in the mass spectrograph inlet system. In addition one can note that the mass 82 peak height is 9% of the mass 80 peak. Since the abundance of S^{34} is 4.2%, this indicates that the mass 80 peak is due to S_2O^+. The 1.6% mass 81 peak also agrees with the 0.74% abundance of S^{33}. The CS_2 may be due to carbon-containing impurities in the generator. The generator had been run for only a short time before the mass spectrograph samples were taken. The CS_2 peaks were about one quarter as strong in the second sample used for mass spectrographic analysis as they were in the first sample. The SO^+ peaks do not indicate the presence of SO in the original sample. The fragmentation of a pure SO_2 sample results in a mass 48 peak which is 34.0% of the mass 64 peak. The observed 35.6% ratio could be explained by the fragmentation of S_2O. It would require a 7% fragmentation for S_2O.

It cannot be said that the absence of a mass 96 peak proves that S_2O_2 is not present in the sample. It is possible that $S_2O_2^+$ fragments 100% into S_2O^+. However, the most probable explanation of the ab-

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(5) A. R. V. Murthy, *Ind. Acad. Sci.*, **36**, 388 (1952).

(6) For more experimental details, see Part I of the Ph.D. thesis of David J. Meschi, University of California, Berkeley, 1956. A microfilm copy may be obtained at nominal cost by addressing the Photographic Laboratory, General Library, University of California, Berkeley 4, California.

(7) F. E. Harris and L. K. Nash, *Anal. Chem.*, **22**, 1552 (1950).

sence of a mass 96 peak is that S_2O_2 is not present in the samples. Since the samples had to be stored for an appreciable period of time before mass spectrographic analysis, it was felt that it would be best to do other types of experiments on fresher samples and not to attempt to further the mass spectrographic analysis.

It was originally observed by Schenk[8] that his nearly pure "sulfur monoxide" samples produced only about a 25% pressure decrease when they were decomposed into SO_2 and sulfur. According to reaction 1 pure SO should have a 50% pressure de-

$$2SO = SO_2 + S(\text{solid}) \qquad (1)$$

crease upon decomposition. Schenk[8] agreed that this fact could be taken as evidence for the existence of some S_2O_2 in his "sulfur monoxide," but it is interesting to note that he suggested that it could be taken as evidence for S_2O in the sample.

In order to determine the stoichiometry of the disulfur monoxide samples, we measured the pressure decrease upon decomposition into sulfur and SO_2 and the SO_2 content before decomposition. If the samples are composed of SO_2 and S_2O then the pressure decrease upon decomposition would be a measure of the S_2O content as given by reaction 2.

$$2S_2O = SO_2 + 3S(\text{solid}) \qquad (2)$$

This pressure decrease should be equal to one-half the difference between the total pressure and the partial pressure of SO_2. If the samples are composed of SO_2 and SO then these same conditions would be met, but Schenk's analysis of a 1:1 sulfur to oxygen ratio would not be satisfied. However, if the samples are composed of SO_2, SO and S_2O_2 then the pressure decrease upon decomposition should be smaller than one-half the difference between the total pressure and the SO_2 pressure.

The ultraviolet analysis of several samples gave an average SO_2 content of 61% when the total pressure was near 100 μ. The difference between the total pressure and the partial pressure of SO_2 in three samples was 50, 54 and 43 μ. The pressure decrease upon decomposition in these samples was 25, 27 and 21 μ, respectively. It is evident that very little S_2O_2 was present in the samples.

The results of gaseous effusiometer measurements of some disulfur monoxide samples are given in Table II. The average molecular weights of the samples are calculated from the effusiometer half times, γ. Using an SO_2 calibration one obtains

$$M(\text{av}) = 64\left(\frac{\gamma}{\gamma(SO_2)}\right)^2 \qquad (3)$$

The half-times γ were obtained by a least squares fitting of the logarithm of the pressure plotted against the effusion time. Over the pressure range measured the best fit was given by a straight line. This is expected when the molecular weights of all the constituents are of similar value. If the molecular weight of the unknown constituent is similar to that of SO_2 then it can be calculated using

$$M(\text{unk}) = \frac{M(\text{av}) - 64X(SO_2)}{1 - X(SO_2)} \qquad (4)$$

where $X(SO_2)$ is the mole fraction of SO_2.

TABLE II

MOLECULAR WEIGHT DETERMINATIONS

Sample	P (total)[a]	$P(SO_2)$[a]	M(av)	M(unk)
38	118.5	47.5	72.7	78.9
39	131	48.5	74.6	80.8
40	121.5	47[b]	71.4	76.1[b]
42	159.5	79.5	71.0	78.0

[a] Pressure in microns. [b] These values are more uncertain because of experimental difficulties.

It can be seen from Table II that M(unk) is, within the experimental uncertainty of one or two units, equal to a value of 80. This is the value of the molecular weight of S_2O. If SO and S_2O_2 were present in the proper ratio to provide an M(unk) value of 80 we would not have obtained linear effusion curves. It is interesting to observe that Schenk[8] obtained an M(av) value between 70 and 71 utilizing a different method. This is in good agreement with our determinations.

Discussion

All three of the experimental techniques are in agreement that S_2O_2 is not present in appreciable quantities in Schenk's "sulfur monoxide." The mass spectrographic and molecular weight determinations are strong evidence for disulfur monoxide, S_2O, as the major constituent. The ultraviolet analysis for SO_2 enables one to see that a sulfur to oxygen ratio of 1:1 is due to the presence of S_2O and SO_2 in nearly equal quantities. While it is possible that the molecule SO is present in small quantities there is no direct evidence of it. The diffuse nature of the ultraviolet spectrum[2,3] can be explained as due to the large number of rotational states possessed by the asymmetric top, S_2O. The 1165 and 679 cm.$^{-1}$ infrared absorption reported by Jones[3] can be assigned as sulfur-oxygen and sulfur-sulfur stretching frequencies of an S-S-O type molecule. Both microwave and infrared measurements will be the subject of a later paper.

The chemical reaction of disulfur monoxide with aqueous alkali is quite complex. Murthy[5] reports that S, $S^{=}$, $S_2O_3^{=}$ and $SO_3^{=}$ result from the reaction with 2 N NaOH. The $SO_3^{=}$ is primarily the result of the SO_2 that is present, while the S, $S^{=}$ and $S_2O_3^{=}$ result from the disproportionation of S_2O. Murthy has shown that the $S_2O_3^{=}$, $S^{=}$ ratio is greatly dependent upon experimental conditions indicating competing reactions. The approximate S_2O_2 concentrations calculated by Murthy on the basis of the $S_2O_3^{=}$ produced is strongly dependent upon assumptions concerning the relative ratio of these competing reactions. On the basis of our work it does not appear to be a valid calculation.

The small amount of stoichiometric data presented by Kondrat'eva and Kondrat'ev[2] supporting the existence of S_2O_2 are difficult to evaluate. They give almost no experimental details, and one is not sure, for example, that they heated and cooled their sulfur residues a sufficient number of times to completely liberate the SO_2. The empirical formula for $S_x\,O_y$ evaluated by these authors is a sensitive function of their data and so it is possible that a small experimental error made them miss the presence of S_2O. In addition Schenk has shown that their data could be interpreted as confirming the

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(8) P. W. Schenk, *Z. anorg. allgem. Chem.*, **248**, 297 (1941).

presence of SO. It seems clear that there is no incontrovertible data to support the existence of S_2O_2.

The salient feature which has led the majority of workers to believe in the presence of SO in the discharge product is the apparent 1:1 sulfur to oxygen ratio. It was only in his later work that Schenk was able to construct a reliable manometer and observe the anomalous 25% pressure decrease upon decomposition into sulfur and SO_2. In order to explain this apparent stoichiometery it would seem reasonable to assume that SO emerges from the discharge tube and polymerizes according to

$$3SO = S_2O + SO_2 \qquad (5)$$

However, from their observation of a negligible pressure change in the discharge products, Evans, Scott and Huston[9] have established that such a polymerization must occur in a period of less than 3 seconds after leaving the discharge tube. In another experiment[10] an attempt was made to observe the ultraviolet absorption due to SO in the products which were rapidly pumped out of a discharge tube. No SO absorption could be detected. However, from the recent work of St. Pierre and Chipman[11] it is now definitely known that SO is stable in a sulfur-rich system near 1,000°. So that if one considers a discharge tube and a low pressure flame to have a high effective temperature then it is reasonable to consider SO as the primary discharge product, despite the fact that there is no direct evidence for it.

It should be pointed out that in a few cases (see Table I of reference 9 and Table II of this paper) a product is obtained which is apparently definitely over 50% in S_2O. This can be interpreted as due to the reaction

$$SO + S_x = S_2O + S_{x-1} \qquad (6)$$

It would also be possible that in the discharge oxygen atoms could be considered as the primary discharge product. In this case both SO and S_2O could result from the capture of oxygen atoms by sulfur molecules much as ozone is formed in the pure oxygen system. If this were the case then the apparent 1:1 sulfur to oxygen ratio would only be a coincidence of kinetic factors.

A third possibility rests on the unknown thermodynamic stability of S_2O. It is clear that S_2O is unstable at room temperature and at temperatures only slightly above room temperature. It is possible, however, that S_2O may be a stable species at elevated temperatures. In either case the thermodynamic stability of S_2O should be investigated and its importance in the sulfur-oxygen system established.

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[9] E. Evans, A. Scott and J. Huston, THIS JOURNAL, **74**, 5525 (1952).

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[CONTRIBUTION NO. 86 FROM THE CRYOGENIC LABORATORY OF THE PENNSYLVANIA STATE UNIVERSITY]

Heat Capacity and Magnetic Susceptibility of Vanadium(III) Ammonium Alum from 1.1 to 20°K.

BY J. J. FRITZ AND H. L. PINCH[1]

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The heat capacity and magnetic susceptibility of vanadium(III) ammonium alum have been measured (in zero magnetic field) from 1.1 to 20°K. The heat capacities show a distinct Schottky transition. This is explained by the assumption that the lowest set of energy levels of the vanadium ion are a singlet and a doublet, with a separation of 4.9 cm.$^{-1}$. The magnetic susceptibilities are substantially in accord with previous less extensive measurements.

Introduction

The magnetic behavior at low temperatures of vanadium(III) ammonium alum is distinctly different from that of the paramagnetic alums of chromium, iron and titanium(III). Despite the fact that vanadium alum possesses the high crystalline symmetry and great magnetic dilution characteristic of the alum structure, it shows large deviations from ideal behavior. The theoretical reasons for this behavior have been discussed by Siegert[2] and Van Vleck.[3]

The theoretical treatment assumes substantial "quenching" of the orbital magnetic moment due to the $^3F_2$ ground state. As a result, the state is split into seven (2L + 1) orbital states (largely degenerate), each of which is further split into three spin states (a singlet and a doublet separated by an amount δ). The over-all orbital splitting is assigned as about 10^4 cm.$^{-1}$. At low temperatures the only orbital states of consequence are the three lowest; the theory assigns these as a singlet and a doublet with a spacing (Δ) of about 10^3 cm.$^{-1}$.

Siegert[2] analyzed the magnetic susceptibility measurements of Van den Handel and Siegert[4] and concluded that the splitting, δ, between spin levels was about 5 cm.$^{-1}$. The magnitude assigned to the orbital splitting, Δ, depended considerably on the details of the theory.

The heat capacity of the salt below 20°K. provides a direct check on the validity of the assignment of

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[1] Abstracted in part from the Ph.D. thesis of H. L. Pinch.

[2] A. Siegert, *Physica*, **3**, 85 (1936); **4**, 138 (1937).

[3] J. H. Van Vleck, *J. Chem. Phys.*, **7**, 61 (1939).

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