Infrared and Raman Spectra of the Low-Temperature Products from Discharged Sulfur Dioxide

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Abstract: SO_2 was subjected to radiofrequency and microwave electrodeless discharges, and the products were quenched at 20 and 80°K. Through the infrared and Raman spectra of the condensates the following compounds were identified: SO_3, S_2O, S_3, S_4, O_3, and a poly(sulfur oxide). The Raman bands of S_3 indicate that it is a bent molecule, whereas the bands of S_4 suggest that it has a trans structure. The possible mechanisms for the formation of the products are discussed.

Intermediates in the oxidation of sulfur and sulfur-containing compounds are of current interest due to their importance in the formation of SO_2 and SO_3. Unstable oxides such as SO, $(SO)_2$, S_2O, SOO, and SO_4 have been proposed as possible intermediates in the oxidation of sulfur; however, there is some confusion as to the identification of these oxides and to the exact role they play in the oxidation process.[1,2] All of the lower oxides of sulfur, *i.e.*, with the ratio $O:S < 2:1$, are unstable and generally decompose to sulfur and the stable oxides or form polymers. The first such oxide to be subjected to physical measurements was prepared by Schenk[3] who passed SO_2 and sulfur vapor at a high temperature through an electric discharge. He assumed that sulfur monoxide, SO, was formed. Later, Jones[4] measured the infrared and ultraviolet spectrum of this new oxide in the gas phase and suggested that it was S_2O_2. However, more recent measurements of both the infrared[5] and mass[6] spectra indicate that the species is actually S_2O.

Schenk[1] has suggested that electric glow or high frequency discharges should also be effective in producing the lower oxides directly from SO_2; thus, we have been investigating the species produced by subjecting SO_2 and $SO_2 + O_2$ to both radiofrequency and microwave electrodeless discharges. Herein, we report on the infrared spectra of the products condensed at 20 and 80°K and the Raman spectrum of the products condensed at 80°K.

Experimental Section

SO_2 (Matheson) and commercial grade O_2 were vacuum distilled several times prior to being used. In experiments using SO_2 doped with O_2, the desired mixture was prepared by standard manometric procedures. Pure SO_2 or a SO_2–O_2 mixture was passed through a radiofrequency ($\leq$200 W at 10 MHz) or a microwave ($\sim$60 W at 2450 MHz) electrodeless discharge. The "hot" gas was quenched onto a CsI substrate in a conventional liquid N_2 infrared cell, onto a CsI substrate in a Cryotip cell[7] at 20°K, or onto a cold finger of a Raman cell at 80°K. The discharge region was located 5 to 12 cm from the low-temperature substrate. In some of the experiments a pin-hole constriction (0.5 to 4.0 mm in diameter) was inserted between the discharge region and the low-temperature substrate, since it was found that the composition of the condensate was different when a constriction was used. The Raman cell was similar to the conventional liquid N_2 infrared cell except that the substrate consisted of a nickel-plated copper thimble filled with liquid N_2.

Infrared spectra were measured on a Perkin-Elmer Model 521 spectrometer, and Raman spectra were measured using a Spex Industries Model 1401 double monochromator, photon counting detection and a C.R.L. Model 52-A argon ion laser emitting at 4880 or 5145 Å ($\sim$100 mW power at the sample). In some of the experiments grating ghosts were detected in the Raman spectrum, but we found that these could be eliminated by placing a long pass filter (Oriel No. G-772-5400) between the sample and the entrance slits of the monochromator.

Results

Infrared Spectra. Infrared spectra of the products from discharged SO_2 condensed at 20 and 80°K are shown in Figure 1. The discharge and the deposition conditions were identical for the two samples, except that the discharge region was separated from the cold substrate by a pin-hole constriction in the case of the 20°K sample. In the spectrum of the sample at 20°K the strong bands at 1320, 1145, and 522 cm^{-1} are assigned to SO_2 and the ones at 1399, 1385, 1070, and 462 cm^{-1} to SO_3.[8,9] The same bands were observed in the spectrum of the sample at 80°K, but the frequencies and intensities of the SO_3 bands are slightly different. The band at 1034 cm^{-1} is observed only in the spectrum of the 20°K sample, and we assign this band to the antisymmetric stretching mode of O_3. Previously, it has been shown that this is the only strong band of O_3 isolated in inert gas matrices.[10–12] Additional evidence for the assignment of this band is the fact that it appears only at 20°K; at 80°K the band is missing which suggests that O_3 (melting point 80 ± 2°K) is condensing on the colder copper portion of the cell.

There is previous evidence[5,13] that the bands at 1165, 679, and 388 cm^{-1} in the spectrum of the sample at 20°K are due to S_2O. These bands were also observed in some of the samples at 80°K, but they only appeared when a pin-hole construction was placed between the discharge and the cold substrate. By comparing

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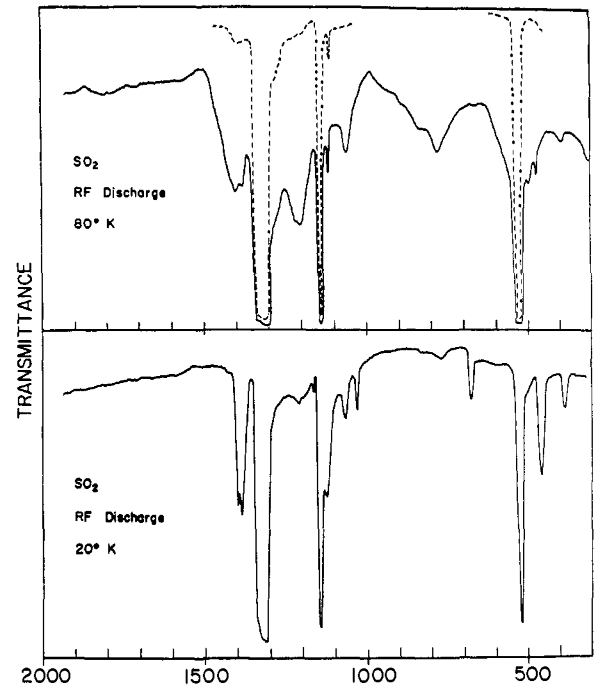

Figure 1. Top: (——) infrared spectrum of the products from discharged SO$_2$ condensed at 80°K; (- - -) infrared spectrum of polycrystalline SO$_2$ condensed at 80°K. Bottom: infrared spectrum of the products from discharged SO$_2$ condensed at 20°K.

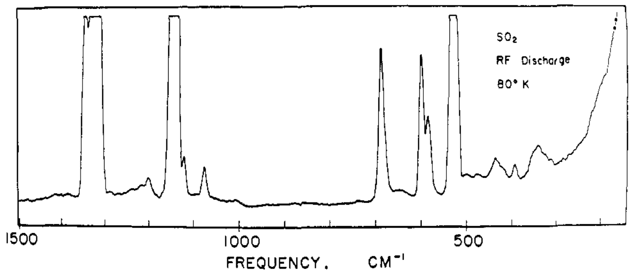

Figure 2. The Raman spectrum of the products from discharged SO$_2$ condensed at 80°K (spectral slit width 5 cm^{-1}).

spectra of many samples deposited under different conditions, we found that the intensity of the band at 1125 cm^{-1} was proportional to the S$_2$O bands. We believe that this band is due to the SO stretching mode of some S$_2$O molecules, and that it is shifted from 1165 to 1125 cm^{-1} through an association of the S$_2$O molecules with SO$_2$; *i.e.*, possibly a S$_2$O–SO$_2$ complex is formed.

The weak bands at 1210 and 775 cm^{-1} in the 20°K spectrum and the stronger bands at 1205, 1065, and 780 cm^{-1} in the 80°K spectrum had the same relative intensities in the spectra of approximately 40 samples; thus, we believe that they belong to the same species and we will discuss its composition after consideration of the Raman spectra. The weak band at 495 cm^{-1} in the 80°K spectrum is the only other spectral feature and we will also discuss its origin later.

Raman Spectra. The Raman spectrum from 100 to 1500 cm^{-1} of the products from discharged SO condensed at 80°K is shown in Figure 2. All of the spectra shown in Figures 2 to 4 were measured using the 5145-Å laser line. We measured several spectra using the 4880-Å laser line and the same bands were observed; however, we also observed an additional series of bands apparently due to a resonance effect, but these will not be considered in this discussion. The three fundamentals of SO$_2$ at 1325, 1145, and 520 cm^{-1} are shown full scale in Figure 2. Three other bands appear in the SO stretching region at 1210, 1075, and 1065 cm^{-1}; these correspond closely to similar bands observed in the infrared spectra. We assign the band at 1075 cm^{-1} to SO$_3$. Relative intensities of the bands in the spectra of ten different samples indicated that the bands at 1210 and 1065 cm^{-1} and the broad band at ~340 cm^{-1} belong to the same species.

There are three strong, sharp bands between 575 and 700 cm^{-1} and several weaker bands between 200 and 700 cm^{-1}. We performed several experiments to determine the origin of the strong bands and their relationship to each other and the other bands in the spectrum. One of the most informative experiments was to warm the condensate in ~50°K increments, recool to 80°K, and remeasure its spectrum. The band at 585 cm^{-1} disappears after the first temperature cycling (80 $\rightarrow$ 130 $\rightarrow$ 80°K), and the bands at 688, 601, and 440 cm^{-1} decrease in intensity. After the next temperature cycling (80 $\rightarrow$ 180 $\rightarrow$ 80°K) the latter three bands disappear. As they disappear bands due to S$_8$ rings appear at 470, 442, and 218 cm^{-1}. We have shown previously[14] that the bands at 442 and 218 cm^{-1} are very characteristic of S$_8$ rings. Plastic sulfur, which consists primarily of long chains, has only a very weak band at 218 cm^{-1} and the 442-cm^{-1} band is replaced with a band at 420 cm^{-1}. A comparison of the spectra before and after the temperature cycling is shown in Figure 3. The fact that sulfur bands appear as the three strong bands disappear leads us to believe that they are due to small sulfur species. The question that remains to be answered is whether or not they are due to the same or different species.

We gained further insight into the origin of these bands by doping SO$_2$ with small amounts of O$_2$ prior to the discharge. Our original intention of performing these experiments was to increase the amount of oxygen containing species. However, this was not the result, since the intensities of the bands in the SO stretching region remained the same whereas some of the other bands increased dramatically. The spectrum of a deposit resulting from the addition of 5% O$_2$ to SO$_2$ is shown in Figure 4a. The intensities of the bands at 651, 585, 495, and 420 cm^{-1} increased considerably, whereas the other bands remained about the same.

Temperature cycling of the condensate again proved very helpful in elucidating its composition. As before, during the first temperature cycling of 50°K the band at 585 cm^{-1} disappeared as did the weaker 651-cm^{-1} band. Also the bands at 688, 601, and 440 cm^{-1} decreased in intensity. As before, bands due to a stable form of sulfur appear in the spectrum; however, this time plastic sulfur was produced. The resulting spectrum after temperature cycling (80 $\rightarrow$ 130 $\rightarrow$ 80°K) is shown in Figure 4b. The band due to sulfur at ~470 cm^{-1} is very strong, a weak band is present at 420 cm^{-1}, and the 218 cm^{-1} band is absent from the spectrum. At a tenfold increase in amplifica-

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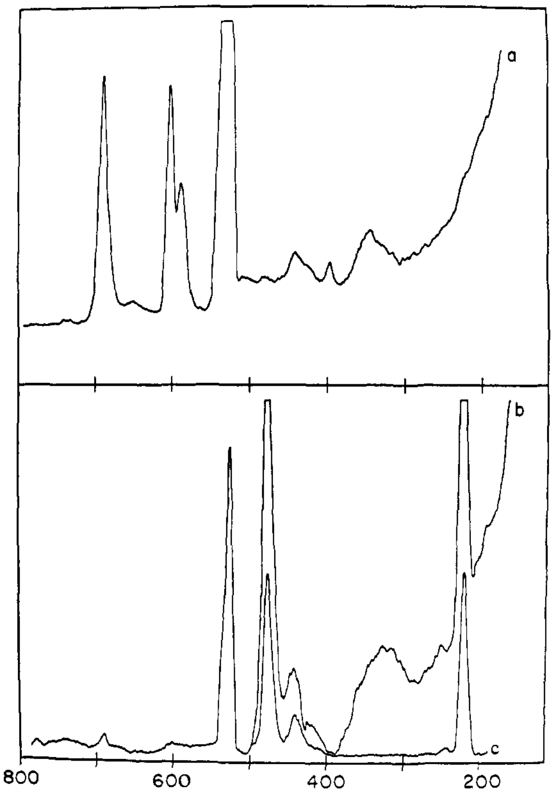


Figure 3. The Raman spectrum of the products from discharged SO_2: (a) deposit at 80°K, (b) deposit after temperature cycling of 80 → 180 → 80°K, (c) deposit after temperature cycling of 80 → 300 → 80°K.

tion the 218-cm^{-1} band due to S_8 rings does appear very weakly as is shown in Figure 4c.

Five experiments were run with SO_2 doped with 1.5 to 10% O_2, and similar results were obtained in all cases. In addition to the increase in the intensities of the bands discussed above, there is an apparent increase in the band at 688 cm^{-1}. At higher resolution it was found that this band is actually a doublet with components at 688 and 680 cm^{-1}; the 680 component can be seen as a shoulder in Figure 4a. The component at 688 cm^{-1} has approximately the same intensity as the band at 601 cm^{-1}. In all of the experiments the bands at 688, 601, and 440 cm^{-1} have the same relative intensities; therefore, they appear to belong to the same molecule. The intensity of the component at 680 cm^{-1} was always proportional to the band at 390 cm^{-1}. Both of these bands are assigned to S_2O.

Effect of CO_2 on the SO_2 Discharge. During these experiments we used several different lecture bottles of SO_2, and we found that older, cast iron lecture bottles generally contained some CO_2 as an impurity. The amount of CO_2 in the lecture bottles varied from 0 to 7% as estimated from the infrared spectrum of the gas in a 10-cm cell. The presence of CO_2 had a great effect upon the amount of SO_3 formed during the discharge experiments; *e.g.*, in a sample with 7% CO_2 present there was an eightfold increase in SO_3. Clearly CO_2 acts as an additional source of oxygen atoms for the oxidation of SO_2 to SO_3.

Discussion

The identities of some of the species present in the condensate from discharged SO_2 are obvious. For example, SO_3 is identified by the doublet at ~1400 cm^{-1}, the sharp band at 465 cm^{-1} in the infrared spectrum, and the sharp Raman band at 1075 cm^{-1}. The presence of O_3 is indicated by the band at 1034 cm^{-1} in the infrared spectrum at 20°K. Furthermore, S_2O is identified by the infrared bands at 1165 (1125 in the SO_2 matrix), 679, and 388 cm^{-1} and by the Raman bands at 680 and 390 cm^{-1}.

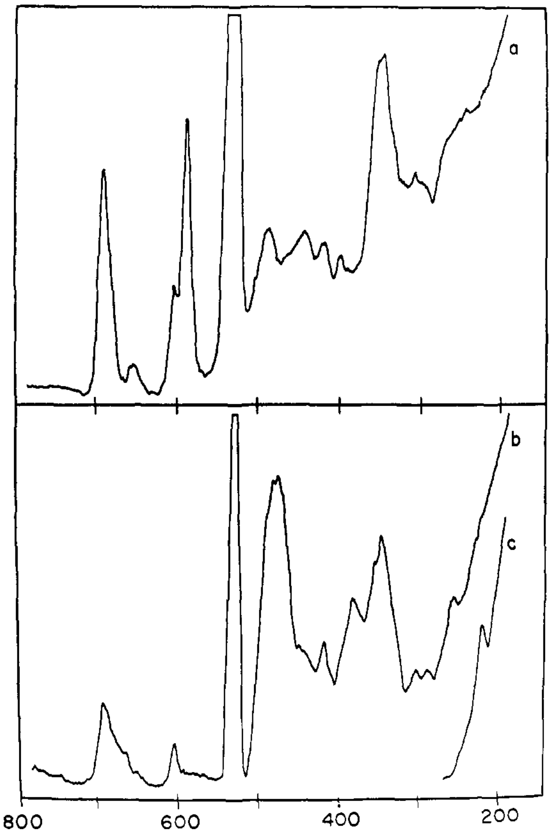


Figure 4. The Raman spectrum of the products from the discharge of 5% O_2 in SO_2: (a) deposit at 80°K, (b) deposit after temperature cycling of 80 → 130 → 80°K, (c) deposit after temperature cycling of 80 → 300 → 80°K with a tenfold increase in amplification (shows the weak band at 218 cm^{-1} due to S_8 rings).

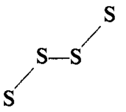
We will now consider the other bands in the spectra. Since the Raman bands between 575 and 700 cm^{-1} are especially prominent and they disappear upon slight warming of the condensate, we believe that they are due to small, reactive sulfur compounds and we will consider their origin first. The sharp band at 585 cm^{-1} and the weak band at 651 cm^{-1} appear and disappear together; thus, we assign them to the same species. When these bands are most intense, plastic sulfur is formed upon warming. This would suggest that the compound consists of an odd number of S atoms since, as we will show later, small species with an even number of sulfur atoms seem to form S_8 rings. After considering the possible reactions which would form sulfur species from a SO_2 discharge and the fact that it goes to plastic sulfur upon warming, we believe that the species is S_3. As shown previously, the bands at 585 and 651 cm^{-1} increased by doping SO_2 with O_2. The addition of O_2 also increases the amount of S_2O. Schenk[1] has suggested that S_2O decomposes by the following reaction

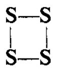
$$2S_2O \longrightarrow 3S + SO_2$$

and we feel that this is the source of S_3. This would explain why the 651- and 585-cm^{-1} bands increase when oxygen is added; *i.e.*, the amount of S_2O is increased and leads to additional S_3.

The frequencies and intensities of the two bands assigned to S_3 suggest that the 651-cm^{-1} band is due to the antisymmetric stretch and the 585-cm^{-1} band to the symmetric stretch. The presence of both bands in the Raman spectrum indicates that the molecule is bent. The bending mode should also be Raman active and it is possible that it gives rise to either the weak band at 490 or 310 cm^{-1} (Figure 4a). During several of the experiments at 80°K we detected weak infrared bands at 650 and 495 cm^{-1}. Possibly these are the antisymmetric stretching and bending modes of S_3, but due to their weak intensities it is difficult to make positive identification. Since sulfur species are very strong Raman scatters, it is possible that the Raman bands due to S_3 can be observed without being able to detect its infrared bands.

The three bands at 688, 601, and 440 cm^{-1} had the same relative intensities in all of the experiments; thus, they appear to belong to the same species. Since S_8 rings form during the warming cycles when these bands are strong, we feel that they are due to a pure sulfur compound with an even number of sulfur atoms (2, 4, or 8) which can easily lead to the formation of S_8 rings. In the matrix-isolated Raman spectrum of S_2 a band was found at 716 cm^{-1};[15] therefore, the present compound could be either S_4 or S_8. Due to the high frequencies of the stronger bands we believe that it is S_4. The fact that we do not observe any of these bands in the infrared spectra suggests that either it is a weak absorber, or that it has a trans or square planar structure, *i.e.*



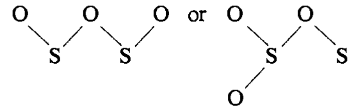


and that the mutual exclusion principle holds. We favor the trans structure, since bands of a square planar structure would probably fall below 500 cm^{-1}. There is a possibility that the 668-cm^{-1} band observed in the matrix-isolated infrared spectrum of high-temperature sulfur[16] is one of the infrared-active fundamentals of this molecule. The reactions to form S_4 probably involve the formation of S_2 in the gas phase and the dimerization of S_2 either in the gas phase or on the matrix surface to form S_4.

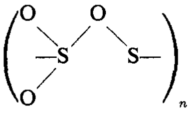
Table I. Observed Frequencies (cm^{-1}) in the Infrared and Raman Spectra of the Products from Discharged SO_2

Ir spectrum 20°K	Ir spectrum 80°K	Raman spectrum, 80°K	Raman spectrum, 80°K, O_2 added	Assignments
1399 m	1402 m			SO_3, ν_3
1385 m	1382 m			
1320 vs	1320 vs	1325 vs	1325 vs	SO_2, ν_3
1210 w–b	1205 m–b	1210 w	1210 w	Poly(sulfur oxide)
1165 vw				S_2O, ν_1
1145 s	1140 s	1145 vs	1145 vs	SO_2, ν_1
1125				S_2O, ν_1 (SO_2 matrix)
	1115 w	1116 w	1115 w	$S^{16}O^{18}O$, ν_1
1070 w	1070 sh	1074 w	1075 w	SO_3, ν_1
	1065 m	1068 sh	1068 sh	Poly(sulfur oxide)
1034 w				O_3, ν_3
775 w–b	840 sh			Poly(sulfur oxide)
	780 m–b			
		668 s	688 m	S_4
679 w		680 sh	680 sh	S_2O, SS stretch
		650 w–b	651 w	S_3, ν_3
		601 s	601 m	S_4
		585 m	585 s	S_3, ν_1
522 s	525 s	525 vs	525 vs	SO_2, ν_2
	495 w	490 w–b	490 w	S_3, ν_2 ?
465 m	468 w			SO_3, ν_2.
		440 w	444 w–b	S_4
			420 w	Poly(sulfur oxide)
388 w	388 w	390 w	391 w	S_2O bending
		342 w–b	350 s	Poly(sulfur oxide)
			310 w	S_3, ν_2 or poly(sulfur oxide)

The three infrared bands at 1205, 1065, and 780 cm^{-1} and the three Raman bands at 1210, 1065, and 342 cm^{-1} appear to belong to the same compound. All of these bands are broad, and we tentatively assign them to a polymer. The bands at 1205 and 1065 cm^{-1} are consistent with antisymmetric and symmetric stretching modes of an SO_2 group, respectively. The infrared band at 780 cm^{-1} and the Raman band at 340 cm^{-1} are in the frequency ranges corresponding to the antisymmetric and symmetric frequencies of an S–O–S group as suggested by Gillespie and Robinson.[17] We could not detect the 780-cm^{-1} band in the Raman spectrum, but this may be due to the fact that it is an antisymmetric stretching mode and only weakly Raman active. Originally, we felt that these bands might be due to a S_2O_3 monomer such as



since the vibrational bands would fit either of these structures and they would account for the reaction of SO with excessive SO_2. However, the broadness of the bands would favor a polymer, possibly of the structure



More information will be needed to determine the exact structure of this compound. However, we have found that it is only stable at low temperatures and that the bands disappear from the spectrum at ~200°K.

The two Raman bands at 350 and 420 cm^{-1} (Figure 4a) are due to either the same or a different polymer. They only appeared in the experiments with O_2 added, and they seem to be strong when S_2O is present in significant amounts. Possibly they are due to a polymer which forms from S_2O. In any event, they also dis-

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appear during the warming cycles; thus, the compound is not stable at room temperature.

The observed frequencies in all of the spectra and the assignments of the bands are summarized in Table I.

Conclusions

The condensed products from discharged SO_2 include the following: SO_3, S_2O, S_3, S_4, O_3, and a poly(sulfur oxide). We can only speculate on the mechanisms for the formation of these compounds in the discharge; however, both our results and those of previous investigations[1,2] suggest that the following reactions are taking place

$$SO_2 \xrightarrow{\text{discharge}} SO, O, S \quad (1)$$

$$SO + SO \longrightarrow (SO)_2 \quad (2)$$

$$(SO)_2 + SO \longrightarrow SO_2 + S_2O \quad (3)$$

$$S_2O + S_2O \longrightarrow S_3 + SO_2 \quad (4)$$

$$S + S \longrightarrow S_2 \quad (5)$$

$$S_2 + S_2 \longrightarrow S_4 \quad (6)$$

$$O + O \longrightarrow O_2 \quad (7)$$

$$O_2 + O \longrightarrow O_3 \quad (8)$$

$$SO_2 + O \longrightarrow SO_3 \quad (9)$$

$$SO_2 + SO \longrightarrow S_2O_3 \quad (10)$$

$$xS_2O_3 \longrightarrow (S_2O_3)_x \quad (11)$$

Not all of these reactions take place in the discharge region or even in the gaseous phase. We believe that reactions 6 and 11 and, to some extent, reactions 4, 8, and 10 are taking place on the matrix surface. In addition, reactions 2 and/or 3 appear to increase by having a constriction between the discharge and the cold substrate. This is demonstrated by the larger amounts of S_2O present when a constriction is used.

One very useful feature of the present experiments is the detection of SO_3 in a mixture by measuring the infrared spectrum of the mixture condensed at liquid N_2 temperature. Calvert and coworkers[18] have pointed out the lack of a spectroscopic method for detecting SO_3 in SO_2 during their photolysis experiments on SO_2. They had to use wet analytical methods for determining the amount of SO_3 present in their experiments. Their method depends upon the converson of SO_3 to SO_4^{-2}, and it assumes that the SO_3 is formed in the gas phase from SO_2 rather than by the oxidation of SO_3^{-2} to SO_4^{-2} in the solution. Using the method described here SO_3 is identified directly.

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Substituent Effects in the Thermodynamics of Hydrogen Bonding as Obtained by Infrared Spectrometry

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Abstract: $\Delta G°$, $\Delta S°$, and $\Delta H°$ have been determined for the formation of the hydrogen bond complex between substituted phenols and dimethylacetamide in carbon tetrachloride. Seventeen monosubstituted phenols were investigated. The linear free energy relation of Hammett is valid with ρ values of 1.95, 1.65, and 1.41 at temperatures -20, $+25$, and $+58°$. The reaction series was found to be essentially isoentropic; measured $\Delta S°$ values fall between -10 and -12 eu. The $\Delta H°$ values varied from -5.6 to -8.2 kcal/mol. The data were obtained from ir spectrometric measurements of the OH stretching frequency. The frequency shift between the OH stretching vibration for free and bonded phenols, $\Delta\nu_{OH}$, is temperature dependent, about -0.6 cm^{-1}/deg. The Badger–Bauer relation, the linear dependence of $\Delta\nu_{OH}$ on $\Delta H°$, is valid. However, the present data are better represented as a linear $\Delta G°/\Delta\nu_{OH}$ relation which gives only one regression line for all temperatures.

This investigation deals with the effect of different substituents on the hydrogen bonding ability of a phenol. The thermodynamic quantities $\Delta G°$, $\Delta H°$, and $\Delta S°$ are determined for the formation of a hydrogen bond complex between a phenolic proton donor and a proton acceptor, the strength of the donor being varied by means of various substituents. The investigation involved 17 different meta- or para-substituted phenols, all complex bonded to the same base, *N,N'*-dimethylacetamide, DMA, in the solvent carbon tetrachloride. The strongest hydrogen bond can be expected to be formed with the carbonyl group.[1] Hydrogen bonds to the nitrogen atom are formed to a much less extent in dilute solutions. Equilibrium constants for the reaction

$$XPhOH + O{=}C(CH_3)N(CH_3)_2 \rightleftharpoons XPhOH\cdots O{=}C(CH_3)N(CH_3)_2 \quad (1)$$

have been obtained through infrared spectrometry. In the ir spectrum of the free phenols the "OH stretch"

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