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

Alfred G. Hopkins, Sheng-yuh Tang, and Chris W. Brown\*

Contribution from the Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881. Received October 20, 1972

Abstract: SO<sub>2</sub> 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<sub>3</sub>, S<sub>2</sub>O, S<sub>3</sub>, S<sub>4</sub>, O<sub>3</sub>, and a poly(sulfur oxide). The Raman bands of S<sub>3</sub> indicate that it is a bent molecule, whereas the bands of S<sub>4</sub> suggest that it has a trans structure. The possible mechanisms for the formation of the products are discussed.

ntermediates in the oxidation of sulfur and sulfurcontaining compounds are of current interest due to their importance in the formation of  $SO_2$  and  $SO_3$ . Unstable oxides such as SO, (SO)<sub>2</sub>, S<sub>2</sub>O, SOO, and SO<sub>4</sub> 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.<sup>1,2</sup> 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<sup>3</sup> who passed SO<sub>2</sub> and sulfur vapor at a high temperature through an electric discharge. He assumed that sulfur monoxide, SO, was formed. Later, Jones<sup>4</sup> measured the infrared and ultraviolet spectrum of this new oxide in the gas phase and suggested that it was S<sub>2</sub>O<sub>2</sub>. However, more recent measurements of both the infrared<sup>5</sup> and mass<sup>6</sup> spectra indicate that the species is actually  $S_2O$ .

Schenk<sup>1</sup> has suggested that electric glow or high frequency discharges should also be effective in producing the lower oxides directly from SO<sub>2</sub>; 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**

SO2 (Matheson) and commercial grade O2 were vacuum distilled several times prior to being used. In experiments using SO<sub>2</sub> doped with O<sub>2</sub>, the desired mixture was prepared by standard manometric procedures. Pure SO<sub>2</sub> or a SO<sub>2</sub>-O<sub>2</sub> 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 N2 infrared cell, onto a CsI substrate in a Cryotip cell<sup>7</sup> 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 be-

tween 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 N2 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<sub>2</sub> 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<sup>-1</sup> to  $SO_{3}$ .<sup>8,9</sup> The same bands were observed in the spectrum of the sample at 80°K, but the frequencies and intensities of the SO3 bands are slightly different. The band at 1034 cm<sup>-1</sup> is observed only in the spectrum of the 20°K sample, and we assign this band to the antisymmetric stretching mode of O<sub>3</sub>. Previously, it has been shown that this is the only strong band of O3 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<sub>3</sub> (melting point  $80 \pm 2^{\circ}$ K) is condensing on the colder copper portion of the cell.

There is previous evidence<sup>5,13</sup> that the bands at 1165, 679, and 388  $cm^{-1}$  in the spectrum of the sample at  $20^{\circ}$ K are due to S<sub>2</sub>O. 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<sub>2</sub> condensed at  $80^{\circ}K$ ; (---) infrared spectrum of polycrystalline SO<sub>2</sub> condensed at  $80^{\circ}K$ . Bottom: infrared spectrum of the products from discharged SO<sub>2</sub> condensed at  $20^{\circ}K$ .

spectra of many samples deposited under different conditions, we found that the intensity of the band at 1125 cm<sup>-1</sup> was proportional to the S<sub>2</sub>O bands. We believe that this band is due to the SO stretching mode of some S<sub>2</sub>O molecules, and that it is shifted from 1165 to 1125 cm<sup>-1</sup> through an association of the S<sub>2</sub>O molecules with SO<sub>2</sub>; *i.e.*, possibly a S<sub>2</sub>O–SO<sub>2</sub> complex is formed.

The weak bands at 1210 and 775 cm<sup>-1</sup> in the 20°K spectrum and the stronger bands at 1205, 1065, and 780 cm<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup> 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<sub>2</sub> at 1325, 1145, and 520 cm<sup>-1</sup> are shown full scale in Figure 2. Three other bands appear in the SO stretching region at 1210, 1075, and 1065 cm<sup>-1</sup>; these correspond closely to similar bands observed in the infrared spectra. We assign the band at 1075  $cm^{-1}$  to SO<sub>3</sub>. Relative intensities of the bands in the spectra of ten different samples indicated that the bands at 1210 and 1065 cm<sup>-1</sup> and the broad band at  $\sim$  340 cm<sup>-1</sup> belong to the same species.



Figure 2. The Raman spectrum of the products from discharged  $SO_2$  condensed at 80°K (spectral slit width 5 cm<sup>-1</sup>).

and 700 cm<sup>-1</sup> and several weaker bands between 200 and 700 cm<sup>-1</sup>. 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  $\sim 50^{\circ}$ K increments. recool to 80°K, and remeasure its spectrum. The band at 585 cm<sup>-1</sup> disappears after the first temperature cycling (80  $\rightarrow$  130  $\rightarrow$  80°K), and the bands at 688, 601, and 440 cm<sup>-1</sup> decrease in intensity. After the next temperature cycling  $(80 \rightarrow 180 \rightarrow 80^{\circ} \text{K})$  the latter three bands disappear. As they disappear bands due to  $S_8$  rings appear at 470, 442, and 218 cm<sup>-1</sup>. We have shown previously<sup>14</sup> that the bands at 442 and 218 cm<sup>-1</sup> are very characteristic of S<sub>8</sub> 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<sup>-1</sup>. 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<sub>2</sub> with small amounts of O<sub>2</sub> 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<sub>2</sub> to SO<sub>2</sub> is shown in Figure 4a. The intensities of the bands at 651, 585, 495, and 420 cm<sup>-1</sup> 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<sup>-1</sup> disappeared as did the weaker 651-cm<sup>-1</sup> band. Also the bands at 688, 601, and 440 cm<sup>-1</sup> 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<sup>-1</sup> is very strong, a weak band is present at 420 cm<sup>-1</sup>, and the 218 cm<sup>-1</sup> band is absent from the spectrum. At a tenfold increase in amplifica-

There are three strong, sharp bands between 575

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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  $80 \rightarrow 180 \rightarrow 80^{\circ}K$ , (c) deposit after temperature cycling of  $80 \rightarrow 300 \rightarrow 80^{\circ}K$ .

tion the 218-cm<sup>-1</sup> band due to  $S_8$  rings does appear very weakly as is shown in Figure 4c.

Five experiments were run with SO<sub>2</sub> doped with 1.5 to 10% O<sub>2</sub>, 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<sup>-1</sup>. At higher resolution it was found that this band is actually a doublet with components at 688 and 680 cm<sup>-1</sup>; the 680 component can be seen as a shoulder in Figure 4a. The component at 688 cm<sup>-1</sup> has approximately the same intensity as the band at 601 cm<sup>-1</sup>. In all of the experiments the bands at 688, 601, and 440 cm<sup>-1</sup> have the same relative intensities; therefore, they appear to belong to the same molecule. The intensity of the component at 680 cm<sup>-1</sup> was always proportional to the band at 390 cm<sup>-1</sup>. Both of these bands are assigned to S<sub>2</sub>O.

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



Figure 4. The Raman spectrum of the products from the discharge of 5% O<sub>2</sub> in SO<sub>2</sub>: (a) deposit at 80°K, (b) deposit after temperature cycling of  $80 \rightarrow 130 \rightarrow 80$ °K, (c) deposit after temperature cycling of  $80 \rightarrow 300 \rightarrow 80$ °K with a tenfold increase in amplification (shows the weak band at 218 cm<sup>-1</sup> due to S<sub>8</sub> rings).

condensate from discharged SO<sub>2</sub> are obvious. For example, SO<sub>3</sub> is identified by the doublet at  $\sim$ 1400 cm<sup>-1</sup>, the sharp band at 465 cm<sup>-1</sup> in the infrared spectrum, and the sharp Raman band at 1075 cm<sup>-1</sup>. The presence of O<sub>3</sub> is indicated by the band at 1034 cm<sup>-1</sup> in the infrared spectrum at 20°K. Furthermore, S<sub>2</sub>O is identified by the infrared bands at 1165 (1125 in the SO<sub>2</sub> matrix), 679, and 388 cm<sup>-1</sup> and by the Raman bands at 680 and 390 cm<sup>-1</sup>.

We will now consider the other bands in the spectra. Since the Raman bands between 575 and 700 cm<sup>-1</sup> 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<sup>-1</sup> and the weak band at 651 cm<sup>-1</sup> 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<sub>8</sub> rings. After considering the possible reactions which would form sulfur species from a SO<sub>2</sub> 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<sub>2</sub> with O2. The addition of O2 also increases the amount of  $S_2O$ . Schenk<sup>1</sup> has suggested that  $S_2O$  decomposes

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

and we feel that this is the source of  $S_3$ . This would explain why the 651- and 585-cm<sup>-1</sup> 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<sup>-1</sup> band is due to the antisymmetric stretch and the 585-cm<sup>-1</sup> 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<sup>-1</sup> (Figure 4a). During several of the experiments at 80°K we detected weak infrared bands at 650 and 495 cm<sup>-1</sup>. 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<sub>3</sub> can be observed without being able to detect its infrared bands.

The three bands at 688, 601, and 440 cm<sup>-1</sup> 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<sup>-1</sup>;<sup>15</sup> 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<sup>-1</sup>. There is a possibility that the 668-cm<sup>-1</sup> band observed in the matrix-isolated infrared spectrum of high-temperature sulfur<sup>16</sup> is one of the infrared-active fundamentals of this molecule. The reactions to form S<sub>4</sub> probably involve the formation of S<sub>2</sub> in the gas phase and the dimerization of S<sub>2</sub> either in the gas phase or on the matrix surface to form S<sub>4</sub>.

The three infrared bands at 1205, 1065, and 780 cm<sup>-1</sup> and the three Raman bands at 1210, 1065, and 342 cm<sup>-1</sup> 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<sup>-1</sup> are consistent with antisymmetric and symmetric stretching modes of an SO<sub>2</sub> group, respectively. The infrared band at 780 cm<sup>-1</sup> and the Raman band at 340 cm<sup>-1</sup> are in the frequency ranges corresponding

**Table I.** Observed Frequencies  $(cm^{-1})$  in the Infrared and Raman Spectra of the Products from Discharged SO<sub>2</sub>

Ir spec- trum 20°K	Ir spec- trum 80°K	Raman spec- trum, 80°K	Raman spectrum, 80°K, O <sub>2</sub> added	Assignments
1399 m)	1402 m)			SO: 72
1385 m)	1382 mJ			503, 73
1320 vs	1320 vs	1325 vs	1325 vs	$SO_2, \nu_3$
1210 w-b	1205 m-b	1210 w	1210 w	Poly(sulfur oxide)
1165 vw				$S_2O, \nu_1$
1145 s	1140 s	1145 vs	1145 vs	$SO_2, \nu_1$
1125				$S_2O, \nu_1 (SO_2 matrix)$
	1115 w	1116 w	1115 w	$S^{16}O^{18}O, \nu_1$
1070 w	1070 sh	1074 w	1075 w	$SO_3, \nu_1$
	1065 m	1068 sh	1068 sh	Poly(sulfur oxide)
1034 w				$O_3, \nu_3$
775 w-b	840 sh 780 m-b			Poly(sulfur oxide)
	,	668 s	688 m	$S_4$
679 w		680 sh	680 sh	S <sub>2</sub> O, SS stretch
		650 w-b	651 w	$S_{3}, \nu_{3}$
		601 s	601 m	$S_4$
		585 m	585 s	$S_{3}, \nu_{1}$
522 s	525 s	525 vs	525 vs	$SO_2, \nu_2$
	495 w	490 w-b	490 w	$S_3, \nu_2$ ?
465 m	468 w			$SO_3, \nu_2$
		440 w	444 w-b	$S_4$
			420 w	Poly(sulfur oxide)
388 w	388 w	390 w	391 w	S <sub>2</sub> O bending
		342 w-b	350 s	Poly(sulfur oxide)
			310 w	$S_2$ , $\nu_2$ or poly- (sulfur oxide)

to the antisymmetric and symmetric frequencies of an S–O–S group as suggested by Gillespie and Robinson.<sup>17</sup> We could not detect the 780-cm<sup>-1</sup> 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<sub>2</sub>O<sub>3</sub> 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  $\sim 200^{\circ}$ K.

The two Raman bands at 350 and 420 cm<sup>-1</sup> (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<sup>1,2</sup> suggest that the following reactions are taking place

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

$$SO + SO \longrightarrow (SO)_2$$
 (2)  
(SO),  $\pm SO \longrightarrow SO_2 \pm SO_2$  (3)

$$(SO)_2 + SO \longrightarrow SO_2 + S_2O \qquad (3)$$
$$S_2O + S_2O \longrightarrow S_3 + SO_2 \qquad (4)$$

$$S_2O + S_2O \longrightarrow S_3 + SO_2 \tag{4}$$
$$S + S \longrightarrow S_2 \tag{5}$$

$$\mathbf{S}_{2}^{\prime} + \mathbf{S}_{2}^{\prime} \longrightarrow \mathbf{S}_{4}^{\prime} \tag{6}$$

$$O + O \longrightarrow O_2 \tag{7}$$

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

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

$$SO_2 + SO \longrightarrow S_2O_2$$
 (10)

$$xS_2O_3 \longrightarrow (S_2O_3)_x \tag{11}$$

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<sub>3</sub> in a mixture by measuring the infrared spectrum of the mixture condensed at liquid N<sub>2</sub> temperature. Calvert and coworkers<sup>18</sup> have pointed out the lack of a spectroscopic method for detecting SO<sub>3</sub> in SO<sub>2</sub> during their photolysis experiments on SO<sub>2</sub>. They had to use wet analytical methods for determining the amount of SO<sub>3</sub> present in their experiments. Their method depends upon the converson of SO<sub>3</sub> to SO<sub>4</sub><sup>-2</sup>, and it assumes that the SO<sub>3</sub> is formed in the gas phase from SO<sub>2</sub> rather than by the oxidation of SO<sub>3</sub><sup>-2</sup> to SO<sub>4</sub><sup>-2</sup> in the solution. Using the method described here SO<sub>3</sub> is identified directly.

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

### Birgitta Stymne, Hans Stymne, and Gunnar Wettermark\*

Contribution from the Royal Institute of Technology, Division of Physical Chemistry, S-100 44 Stockholm, Sweden. Received October 2, 1972

Abstract:  $\Delta G^{\circ}$ ,  $\Delta S^{\circ}$ , and  $\Delta H^{\circ}$  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  $\rho$  values of 1.95, 1.65, and 1.41 at temperatures -20, +25, and  $+58^{\circ}$ . The reaction series was found to be essentially isoentropic; measured  $\Delta S^{\circ}$  values fall between -10 and -12 eu. The  $\Delta H^{\circ}$  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<sup>-1</sup>/deg. The Badger-Bauer relation, the linear dependence of  $\Delta \nu_{OH}$  on  $\Delta H^{\circ}$ , is valid. However, the present data are better represented as a linear  $\Delta G^{\circ}/\Delta \nu_{OH}$  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  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$ , and  $\Delta S^{\circ}$  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.<sup>1</sup> Hydrogen bonds to the nitrogen atom are formed to a much less extent in dilute solutions. Equilibrium constants for the reaction

$$XPhOH + O = C(CH_3)N(CH_3)_2$$

 $XPhOH \cdots O = C(CH_3)N(CH_3)_2 \quad (1)$ 

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

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