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DISULFUR MONOXIDE III.
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Disulfur Monoxide III. Its Infrared Spectrum and Thermodynamic Functions

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Abstract

A study of the infrared spectrum of frozen films of S_2O has led to a complete infrared assignment including the bending frequency at 388 ± 2 cm^{-1}. The thermodynamic functions $(F° - H_0°)/T$ and $(H° - H_0°)/T$ for gaseous S_2O are tabulated from 273.15 - 3,000°K. Estimates of the standard enthalpy of formation for gaseous S_2O are given and its thermodynamic stability is discussed.

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Introduction

Now that disulfur monoxide, S_2O, is a well established molecular species,[1] its chemical and physical properties can be studied. Current work is being done on its chemical reactions.[2] This paper is concerned with its thermodynamic properties and an assignment of its vibration spectrum. A previous determination of the standard enthalpy of formation of S_2O has been obtained from ionization potentials,[3] but since this is only an approximate minimum value, other possible values will be discussed.

(1a) I. D. J. Meschi and R. J. Myers, J. Am. Chem. Soc. 78, 6220 (1956).

(1b) II. D. J. Meschi and R. J. Myers, J. Molec. Spec. 3, 405 (1959).

(2) P. W. Schenk and R. Steudel, Angew. Chem. 75, 793 (1963); P. W. Schenk and W. Holst, Z. anorg. allgem. chem. 319, 337 (1963).

(3) R. Hagemann, Compt. Rend. 255, 1102 (1962).

Experimental

The samples of S_2O, containing about 50% SO_2, were prepared by the usual discharge method.[1] For our infrared studies the samples were sprayed on a salt window cooled to 77°K in a low temperature cell.[4] To study the decomposition of S_2O several spectra were taken after the window had been allowed to warm to 100°K and to 280°K, but the spectra were always taken after the window was cooled back to 77°K. These spectra were taken several years ago on a modified Perkin-Elmer model 12C single beam instrument utilizing either KBr or CsI optics. The wave length scale in the CsI region was determined from the water bands that appeared in the background of the single beam instrument.

Infrared Results

In the region from 600 - 1400 cm^{-1} two bands were observed in the frozen films which could be ascribed to S_2O. The frequencies of these bands were identical, within our resolution, to the 679 and 1165 cm^{-1} found by Jones[5] in the gas phase. The 1165 cm^{-1} band is close to an SO_2 absorption[6] and the two could never be entirely resolved. The

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(4) E. D. Becker and G. C. Pimentel, J. Chem. Phys. 25, 224 (1956).

(5) A. V. Jones, J. Chem. Phys. 18, 1263 (1950).

(6) R. N. Wiener and E. R. Nixon, J. Chem. Phys. 25, 175 (1956); P. A. Giguère and M. Falk, Can. J. Chem. 34, 1833 (1956).

679 cm^{-1} absorption is completely free of SO_2 absorption. When the salt window was warmed to 100°K the S_2O bands at 1165 and 679 cm^{-1} decreased greatly. After warming to 280°K the 679 cm^{-1} band could not be observed but an absorption of about one-third original intensity remained at 1130 cm^{-1}. These observations are consistent with diffusion of S_2O in an SO_2 matrix at 100°K followed by decomposition into SO_2 and sulfur. Since the band near 1100 cm^{-1} can be ascribed to an S-O stretch, it is clear, as observed by Schenk,[7] that some oxygen remains bonded to the produced sulfur at temperatures as high as 280°K.

Since S_2O is a bent triatomic molecule it should have two stretching and one bending frequency. The 1165 and 679 cm^{-1} can be readily assigned to the two stretches and the bend would normally be found at a lower frequency. A measurement of microwave satellite intensities[1b] gave a value of 370 ± 30 cm^{-1} for the lowest frequency vibration for S_2O, and the spectroscopic temperature coefficient measurements[8] indicate that there is a frequency of about 450 cm^{-1}. In the range from 300 - 450 cm^{-1} a single S_2O band was found at 388 ± 2 cm^{-1} in a frozen film at 77°K. This band had the same warm-up characteristics as did the 679 cm^{-1} absorption. The bending frequency in the gas phase would be expected to differ from 388 cm^{-1} by less than 10 cm^{-1}.

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(7) P. W. Schenk, Z. anorg. allgem. chem. 248, 297 (1941).

(8) E. Kondrat'eva and V. Kondrat'ev, J. Phys. Chem. U.S.S.R. 14, 1528 (1940).

Thermodynamic Functions

On the basis of the infrared measurements in this paper and the previous work[5] we know without doubt all three fundamental vibrational frequencies for S_2O. The microwave work[1b] has also supplied the rotational constants and the symmetry (C_s). The thermodynamic functions for gaseous S_2O on the basis of a rigid rotor, harmonic oscillator model were calculated from these data and they are listed in Table I.

Thermodynamic Stability

S_2O, called "sulfur monoxide" or "S_2O_2" in the older literature, has been produced in a variety of nonequilibrium systems[1a, 9]. Possibly it is present in significant amounts in those high temperature oxygen-sulfur equilibria which are rich in sulfur. For a study of the thermodynamic stability of S_2O in these and similar systems the standard enthalpy of formation ΔH°_0 [$2S(rh) + \frac{1}{2}O_2(g) \rightarrow S_2O(g)$, at 0°K] is needed. In the absence of a direct measurement an estimated ΔH°_0 would be useful.

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(9) R. G. W. Norrish and G. A. Oldershaw, Proc. Roy. Soc. (London), A249, 498 (1959);
R. G. W. Norrish and A. P. Zeelenberg, Proc. Roy. Soc. (London), A240, 293 (1957);
A. L. Myerson, F. R. Taylor, and P. L. Hanst, J. Chem. Phys. 26, 1309 (1957).

An approximate value for ΔH°_0 can be based on bond energies. The corresponding bond distances and angles in S_2, SO, S_2O, and SO_2 are similar.[1b, 10] Furthermore, the bond dissociation energies Do(S-O) and Do(OS-O) are nearly equal.[11] These observations imply that Do(S-S) and Do(S-O) may be used to calculate ΔH°_0 for S_2O. With these assumptions a $\Delta H^\circ_0 = -34$ Kcal/mole is obtained. From measurements of ionization potentials, ultraviolet spectrum, and equilibria in sulfur-oxygen system experimental lower limits for ΔH°_0 can be established. These limits indicate that S_2O is less stable than is indicated by the bond energy calculation.

Hagemann[3] has measured the appearance potentials of SO^+ from both SO_2 and S_2O. His measurements give a value of 2.0 ± 0.4 e.v. for the energy required to produce $S_2O + O$ from $SO_2 + S$. This value gives a

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(10) P. A. Giguère, J. Phys. Chem. 64, 190 (1960).

(11) All the thermodynamic data are taken from Table I of this paper and Appendix 7 of G. N. Lewis, M. Randall, K. S. Pitzer and L. Brewer, Thermodynamics, McGraw-Hill Book Co., New York 1961. There is some uncertainty about the values of 101 and 123.5 Kcal/mole used for the dissociation energies of S_2 and SO, respectively. See R. Colin, P. Goldfinger and M. Jeunehomme, Nature 187, 408 (1960) also W. D. McGrath and J. F. McGarrey, J. Chem. Phys. 37, 1574 (1962).

ΔH_0° = -17 ± 9 Kcal/mole. Hagemann implies in his paper that this value is a lower limit for ΔH_0°.

In his work on the ultraviolet absorption spectrum of S_2O Jones[5] noted a well defined predissociation limit at 3153.8 A in a progression which starts from the ground vibrational state. This value corresponds to an energy for photodissociation of 90.5 Kcal/mole. If S_2 + O were the products of this dissociation then a minimum ΔH_0° for S_2O would be -1 Kcal/mole. This value seems to be rather too high. If SO + S were the products then a minimum ΔH_0° would be -23 Kcal/mole. These are minimum values because of the unknown amount of excess energy carried off by the products. Excess energy in the form of electronic excitation is unlikely because the first excited states of both the S atom and SO are sufficiently high[12] to give a value for ΔH_0° of about 0 Kcal/mole.

Photodissociation studies of SO_2[13] and NO_2[14] have shown that the excess rotational and vibrational energy of the products can be small.

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(12) The $^1\Delta$ state of SO is not known but its energy should be similar to that found in O_2.

(13) P. Warnek, F. F. Marmo and J. O. Sullivan, J. Chem. Phys. 40, 1132 (1964).

(14) J. N. Pitts, J. H. Sharp and S. I. Chan, J. Chem. Phys. 40, 3655 (1964).

The most complete study of sulfur-oxygen vapor in equilibrium has been done by Dewing and Richardson.[15] They used silver beads in equilibrium with the vapor at 1,000° - 1,500°K. They interpreted their results in terms of the gas phase equilibrium

$$S_2 + 2\ SO_2 = 4\ SO \qquad (1)$$

but the equilibrium

$$3\ S_2 + 2\ SO_2 = 4\ S_2O \qquad (2)$$

may also have been significant. If so, then the relationship between the apparent equilibrium constant calculated by Dewing and Richardson (K_a) and those for equilibria (1) and (2) would be

$$K_a^{\frac{1}{4}} = K_1^{\frac{1}{4}} + 3\ K_2^{\frac{1}{4}}\ P(S_2)^{\frac{1}{2}} \qquad (3)$$

In their experiments the equilibrium pressure of S_2, $P(S_2)$, ranged only from 2.9 to 3.9×10^{-3} atm. Therefore, a variation of K_a would not have been detected even if relatively large amounts of S_2O were present. If we assume that under their experimental conditions equilibrium (2) is dominant then with the help of equation (3) we calculate a value of $\Delta H_0^\circ = -15$ Kcal/mole for S_2O from Dewing and Richardson's data. This value represents a rather well established lower limit for ΔH_0°.

In their silver bead experiments Dewing and Richardson arrived at a value for the ΔH_0° of SO, neglecting equilibrium (2), which can be taken as in error by -3 Kcal/mole (this is the largest error consistent with the accepted values of Do(S-S) and Do(S-O) and their errors[11]). If this

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(15) E. W. Dewing and F. D. Richardson, Trans. Faraday Soc. 54, 679 (1958).

-3 Kcal/mole error is ascribed to equilibrium (2) then equation (3) allows one to calculate a ΔH°_0 = -13 Kcal/mole for S_2O. This value is only slightly larger than the -15 Kcal/mole value which was based upon the complete neglect of equilibrium (1). Since it seems improbable[11] that equilibrium (1) can be neglected the silver bead data of Dewing and Richardson makes the ΔH°_0 = -13 Kcal/mole a realistic lower limit for the heat of formation of S_2O. While the bond energy and predissociation values all indicate a more negative ΔH°_0 value for S_2O the only well established equilibrium data in sulfur-rich systems shows that S_2O can not be more stable than is allowed by a ΔH°_0 = -13 Kcal/mole.

Since S_2O can be produced in relatively high yield in a number of high temperature systems it seems possible that the actual value of ΔH°_0 is fairly close to the lower limit of -13 Kcal/mole. We are aware of only one experiment reported in the literature on which a useful upper limit for ΔH°_0 of S_2O can be based. Schenk[16] reported that S_2O can be prepared in 5% yield (based upon SO_2) by heating SO_2 and sulfur vapor with a Nernst glower. If we assume that Gibbs free energy is an applicable criterion of equilibrium in this case and that the net reaction is given by equation (2), then one can write

$$\Delta F = \Delta F^\circ - RT\ln[P(O_2)^{-2}\, P(S_2)^{-3}\, P(S_2O)^4] \qquad (4)$$

A useful upper limit for ΔH°_0 can be calculated if ΔF is set equal to zero under Schenk's conditions.[16] Schenk does not describe his experimental

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(16) P. W. Schenk, Z. anorg. allgem. chem. 229, 305 (1936).

conditions in great detail, but reasonable assumptions (T~2,000°K and $P(SO_2)^{-2}\ P(S_2)^{-3}\ P(S_2O)^4 \geq 10^{-12}$) give a maximum ΔH°_0 = 2 Kcal/mole. This value is also a reasonable upper limit on the basis of bond energies.

The range that our limits place on the relative importance of SO and S_2O in sulfur rich systems is still rather large. If one assumes that at 1,000°K $P(SO_2) = P(S_2) \doteq 0.5$ atm then $P(SO) \sim 10^{-4}$ atm. If ΔH°_0 for S_2O is -13 Kcal/mole then in this system $P(S_2O) \sim 10^{-2}$ atm, but if ΔH°_0 = 2 Kcal/mole then $P(S_2O) \sim 10^{-6}$ atm. Only further experimental data will be able to remove this uncertainty.

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