[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Photolysis and Extinction Coefficients of Gaseous Carbonyl Sulfide

BY GEORGE S. FORBES AND JAMES E. CLINE

The absorption spectrum of carbonyl sulfide has been described as continuous from λ 2550 Å. to the far ultraviolet.[1] The indicated threshold energy of dissociation is 111 kcal. corresponding[1] to a combination of the processes COS + 76 kcal. → CO + S and S + 35 kcal. → S, ^{1}D. The process COS + 148 kcal. → CS + O is thermodynamically impossible at the beginning of the continuum. Mulliken[2] has employed the above data for interpretation of the electronic structure of carbonyl sulfide. Its photochemical behavior has not been investigated quantitatively, but it has been observed[1] that sulfur is deposited during exposure to ultraviolet light.

The photolysis of gaseous hydrogen sulfide, recently investigated in this Laboratory,[3] had necessitated the development of a cylindrical cell which could be detached from the apparatus and rotated behind the exit slit of a monochromator at successive levels. The sulfur formed as a reaction product was thus distributed over a surface of 120 sq. cm. and was shown to have a negligible effect upon light transmission. This cell proved to be suitable for experiments upon carbonyl sulfide. The train[3] for introduction of the original gas and for measurement of permanent gas produced by photolysis was used, without modification except in the last two experiments. Stopcocks were avoided altogether by free use of capillary inner seals, mercury valves and liquid air. High vacuum technique was consistently employed. But an unexpected retention of carbon monoxide by solid carbonyl sulfide at liquid air temperature called for a procedure more complicated than that found adequate in the previous research.

Extinction coefficients of carbonyl sulfide were not found in the literature. These were needed to predict the minimum pressures which would correspond to adequate absorption, in our cell, of light of suitable wave lengths. Using a Judd Lewis spectrophotometer[4] and a small Hilger quartz spectrograph, the required data were obtained. The fused quartz gas absorption cell, with plane parallel ends, was 4.56 cm. in length, and pressures ranged from 0.3 to 298 mm. In Fig. 1, $\alpha p d = \log I_0/I$ where p is in mm. of mercury referred to 0° , and d in cm. There is clear evidence of a rounded maximum at λ 225 mμ (126 kcal.) and of a sharp maximum at λ 208 mμ (137 kcal.) the existence of which was obvious in many spectra in addition to the one which served for the determination of α at that wave length. The minima occur at λ 214 and 207 mμ, respectively. These features of the spectrum imply transitions not recognized by Lochte-Holtgreven and Bawn.[1] We have thus far been unable to identify them with certainty.

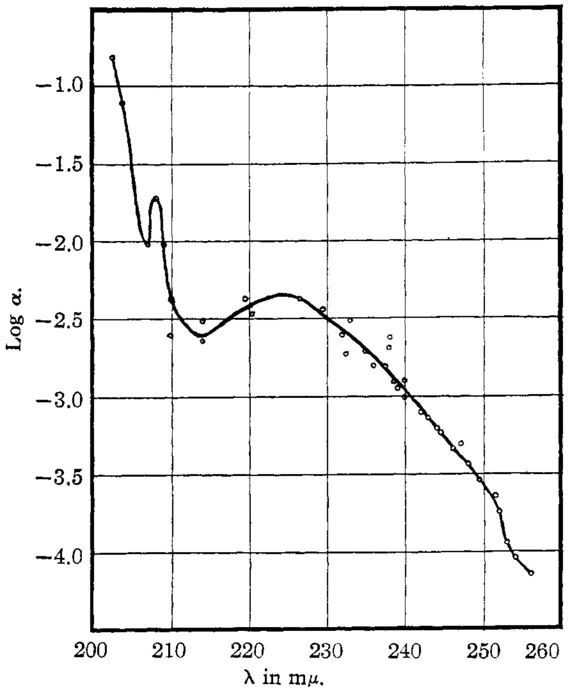

Fig. 1.—Extinction coefficients of carbonyl sulfide.

Carbonyl sulfide was prepared by dropping concentrated C. P. sulfuric acid into a saturated solution of potassium thiocyanate. The gas was washed with 33% sodium hydroxide, then condensed with liquid air into a large trap. This trap was sealed off from the gas generator, and opened into the all-glass distilling system by breaking an inner capillary seal with a magnetic

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(1) Lochte-Holtgreven and Bawn, *Trans. Faraday Soc.*, **28**, 698 (1932).

(2) Mulliken, *J. Phys. Chem.*, **3**, 720 (1935).

(3) Forbes, Cline and Bradshaw, THIS JOURNAL, **60**, 1431 (1938).

(4) Judd Lewis, *J. Chem. Soc.*, **115**, 312 (1919).

hammer. With the carbonyl sulfide still frozen out, the entire system was evacuated on a mercury diffusion pump to a very low pressure. The carbonyl sulfide in its trap was next surrounded with solid carbon dioxide and distilled through a column filled with phosphorus pentoxide on glass wool. The distillate was condensed into small receivers cooled with liquid air, retaining the middle portion only. A second distillation followed before the gas was stored in a two-liter flask, provided with mercury valves as previously described[3] (p. 1433, Fig. 2). The mercury surface in contact with the gas remained bright over the time of the experiments, three months or more, including summer vacation.

Radiations over the range λ 226 to λ 231 mμ, designated below as λ 228 mμ, were isolated, by a prism monochromator, using a constant spark gap[5] between a lower bar of cadmium and an upper bar of aluminum. Radiations, λ 206 to λ 210 mμ, designated below as λ 208 mμ, were obtained using a lower bar of zinc and an upper bar of aluminum. Most of the details of the exposure to light and of the measurement of permanent gas photochemically evolved—assumed to be carbon monoxide—have been described sufficiently.[3]

The results of the first eight experiments appear in Table I. Before tabulation the quanta incident upon the external surface of the call were divided by 1.076 to correct for reflection at the cell walls[3] (p. 1435). Stock, Siecke and Pohland[6] have reported that carbonyl sulfide in contact with finely divided silica is broken down, even at room temperature, into carbon dioxide and carbon disulfide, but absence of permanent gases was not proved. In Experiment 1 carbonyl sulfide remained in the quartz reaction vessel with exclusion of ultraviolet radiation for several weeks, after which the pressure of permanent gas was found to be only 0.002 mm. As this is 10% of the amount found after the average photolysis, in which the gas remains in the cell for a few days only, the thermal (dark) reaction can safely be neglected. Experiments 2 to 8 at first appear unaccountably discordant, as the maximum range of ϕ, 0.49 to 1.38, is thirteen times that observed during the work on hydrogen sulfide,[3] in which an identical experimental procedure was employed.

Table I

Photolyses of Carbonyl Sulfide (First Series)

Expt.	λ	P_{cos}	Quanta (10^{17})	Quanta per sec. (10^{14})	CO, mol. (10^{17})	ϕ corr.	Remarks
1	...	189	0	0	0.5	..	Cell filled
2	208	189	5.22	5.80	3.58	0.69	
3	208	189	4.50	5.01	4.96	1.10	
4	208	430	3.75	4.17	2.63	0.70	Cell filled
5	228	430	13.1	36.5	18.26	1.39	
6	228	1492	9.45	26.3	4.63	0.49	Cell filled
7	228	1492	6.24	8.67	5.46	0.87	
8	228	1492	5.81	8.06	7.12	1.23	

Apparently the variations in ϕ are unrelated to changes in any of the tabulated quantities. On the other hand, a second photolysis of each new sample of gas gives a value of ϕ, higher than the first, and a third (Experiment 8) a value higher still. To explain this trend of ϕ, we entertained the following hypothesis. Some of the carbon monoxide formed by photolysis remained in the tail of the cell at liquid air temperature when the undecomposed carbonyl sulfide was frozen out. This might conceivably occur through occlusion, solution, adsorption or formation of a dipole association compound stable at low temperatures only. A separate investigation of these possibilities might well yield results of interest. Whatever the mechanism, a part of the carbon monoxide formed in one experiment was, in terms of our hypothesis, liberated in the next one so as to make the second quantum yield greater than the first. Table Ia refers ϕ to total quanta and total moles for each of the three samples and leads to values considerably nearer unity.

Table Ia

Combined Photolyses of Carbonyl Sulfide

Expts. combined	Total quanta	Total CO, mol.	ϕ
2, 3	9.72×10^{17}	8.54×10^{17}	0.88
4, 5	16.85	20.89	1.24
6, 7, 8	21.50	17.21	0.80

To test out our hypothesis the following experiment was performed. The quartz reaction cell was filled in the usual manner with carbonyl sulfide at a pressure of 800 mm. The gas was then frozen out, by liquid air, into the tail of the vessel, and the system thoroughly evacuated. From a small tube provided with a capillary inner seal and a magnetic hammer, dried carbon monoxide, separately prepared, was introduced into the cell. Its volume and pressure corresponded to 1.12×10^{-6} mole, about as much as would be formed in an average photolysis. The carbonyl sulfide was allowed to evaporate and to mix with this carbon monoxide, after which it was again

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(5) Forbes and Brackett, This Journal, **53**, 3973 (1931).

(6) Stock, Siecke and Pohland, *Ber.*, **57**, 719 (1924).

condensed with liquid air. The permanent gas remaining, measured in the manner customary after a photolysis, was found to be 0.343×10^{-6} mole, or only 30.6% of the amount introduced. Opening the mercury seal, this carbon monoxide in the gas phase was pumped out, the reaction cell was sealed off, the carbonyl sulfide was again evaporated and condensed. The cell was again connected through an additional capillary seal to the main apparatus, whereupon 0.191×10^{-6} mole of permanent gas was found in the gas phase, or 17.0% of the original admixture. When this procedure was carried out for the third time, 0.342×10^{-6} mole was obtained, that is 30.5% more. So far, 47.5% of the original sample had been recovered from the solid, and 21.9%, apparently, was still retained by it. These data explain the trend of the results shown in Table I and support the hypothesis offered for its explanation.

In this connection it is of interest to note that Pearson and Robinson[7] found difficulty in obtaining samples of carbonyl selenide which did not contain substantial amounts of carbon monoxide. The outcome of Experiment 1 indicates the absence, in our carbonyl sulfide as originally purified, of any serious impurity of carbon monoxide. And since the main supply was condensed and pumped out before each successive sample was taken, any such contamination, no matter how small, must have decreased during the series.

There was one danger in applying the above procedure to the correction of quantitative results. A part of the carbon monoxide retained by carbonyl sulfide might be lost during evacuation of the reaction cell after each successive pressure measurement. In order to preserve all the permanent gas for measurement, a two-liter bulb was attached to the train at such a position that any carbon monoxide not retained by solid carbonyl sulfide expanded into a volume seven times that of the cell just before the pressure was measured. The cell was then sealed off, and all the gas in the flask and McLeod gage was pumped out and rejected. Next the cell was reconnected to the train through a new inner capillary seal. Carbonyl sulfide was evaporated and again frozen out; the capillary seal was broken and the permanent gas still present was again allowed to expand sevenfold. This cycle was carried out three times in Experiment 9 and four times in Experiment 10. A distinct advantage of these operations was that each new condensation of carbonyl sulfide occurred under a carbon monoxide pressure about half that prevailing in the previous condensation.

The optimum amount of carbonyl sulfide would be barely sufficient to absorb about 99% of the light used. The quantities taken in Experiments 9 and 10 were chosen with this end in view. The sample of carbonyl sulfide used in Experiment 10 was condensed and pumped out three times before photolysis, not twice as in the preceding experiments.

TABLE II

PHOTOLYSES OF CARBONYL SULFIDE (SECOND SERIES)

	Quanta	Moles of CO found (10^{17})					ϕ
Expt.	corrected	1	2	3	4	Total	Total
9	7.43×10^{17}	4.25*	1.44*	0.93†		6.62	0.89
10	6.52×10^{17}	3.58*	1.42*	0.67*	0.47†	6.14	0.94

Pressure of COS = 161 mm. λ = 208 mμ.

Table II shows the successive stages in Experiments 9 and 10. Stars denote amounts of permanent gas *rejected*, daggers denote *total* gas present at the time of a *final* pressure measurement. The quantum yields ϕ in the last column, based upon summations of the amounts of gas listed in the previous columns, do not fall far short of unity. If one assumed that the carbonyl sulfide, after final measurement, still retained a quantity of gas equal to that found in this final measurement, the indicated quantum yields would become 1.02 and 1.01, respectively.

The experiments described above indicate that the products of the primary act do not recombine to any important extent, and that the carbon monoxide, at least, does not enter into any other secondary reactions.

Summary

Pure dry gaseous carbonyl sulfide was exposed to light of wave lengths 225 and 208 mμ in an apparatus previously used to measure the quantum yield of hydrogen sulfide. The same procedures and precautions were followed.

Extinction coefficients of carbonyl sulfide were measured from λ 226 to 202.6 mμ. Minima were observed at λλ 214 and 207 mμ, also maxima at λλ 225 and 208 mμ which indicate the importance of transitions not previously recognized.

Quantum yields, ϕ, were calculated as molecules of permanent gas evolved per quantum absorbed; ϕ varied from 0.5 to 0.7 in initial photolyses of three samples, but in subsequent photolyses

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[7] Pearson and Robinson, *J. Chem. Soc.*, 652 (1932).

of these samples ϕ increased to values exceeding unity.

These irregularities were traced to retention of carbon monoxide by solid carbonyl sulfide at liquid air temperature. After suitable modification of the apparatus, most of this retained gas could be recovered in successive portions and measured. Thus corrected, ϕ became 0.9 approximately. Further corrected by means of a reasonable estimate of the traces of gas still retained, ϕ was very close to unity.

This outcome corresponds to the equation $COS + h\nu = CO + S$, in which the states of the products cannot at present be exactly specified. Apparently, recombination of the primary products, and other secondary reactions involving carbon monoxide are negligible.

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[Contribution from Carnegie Institute of Technology]

Studies on Cellulose Compounds

By E. Berl and W. Koerber

The reason for the solution of cellulose esters and ethers in certain solvents has not been discussed very thoroughly up to this time. With the exception of the publications of Highfield[1] and Werner and Engelmann[2] very little material has been published.

It seems that cellulose nitrates are soluble at room temperature in those solvents which have partial valences on oxygen, for example, in ketones like acetone. Completely substituted cellulose triacetates are soluble at room temperature in solvents which, like chloroform or dichloromethane, have partial valences on the carbon. If, besides the bound acetyl groups, unsubstituted OH groups are present in a certain ratio, the solution in ketones with partial valences on the carbonyl oxygen takes place at room temperature.

The influence of temperature on the solubility of cellulose esters has been studied very little. In this publication the solubility of different cellulose nitrates and acetates in fibrous form in different solvents at room temperature and at −50° has been studied. The microphotographs (Figs. 1a, 1b, 1c) which are made with an enlargement of ×436 show the results. The solubility Tables I and II are self-explanatory.

One hundred mg. samples dried over calcium chloride were put into test-tubes and 2 cc. of the organic solvent added. The tubes were kept in a water-bath at 20° for fifteen minutes. Another series of test-tubes with the same samples and solvents was kept in solid carbon dioxide at −50° for fifteen minutes.

The materials were stained with oil red (Du Pont Company) in carbon tetrachloride solution. Before staining, all materials were dried at 100°, then stained on the slide, and dried again.

The effects of the solvents on the materials at the different temperatures are shown in Tables I and II: −, fibers remain insoluble and unchanged; +, fibers have lost their original structure, and form a solid, translucent lump of the same refractive index as the solvent; ++, fibers form a gel at low temperature which consists of small, soft, translucent lumps. This gel does not change its consistency when warmed to room temperature. It is highly swollen and has a limited solubility in the solvent. After standing for a while at room temperature two phases are formed: the viscous gel covered by the nonviscous solvent; +++, fibers are completely dissolved, the viscosity of the solvent is increased; (+) the width of the fibers has been considerably enlarged by swelling.

Table I

Solubility of Cellulose Nitrates

Solvents	°C.	12.02%	12.6%	13.4%	13.9%
Ether	+20	−(2)	−(7)	−(2)	−(30)
	−50	−(3)	−(8)	−(22)	−(31)
Ethanol	+20	−(4)	−(9)	−(23)	−(32)
	−50	++(5)	−(10)	−(24)	−(33)
Ether–ethanol 60:40	+20	+++	+++	−	−(28)
	−50	+++	+++	++(15)	+(29)
Methanol	+20	+++	+++	−(25)	−(34)
	−50	+++	+++	++(26)	++(35)
Glacial acetic acid	+20	+++	+++	−(20)	−
Ethylene glycol	+20	−	−	−	−
Acetic anhydride	+20	+++	++	++	++
Formic acid	+20	−	−	−	−
Ethyl acetate	+20	+++	+++	+++	+++
Methyl acetate	+20	+++	+++	(+)	(+)
	−50	+++	+++	+++	+++

Table II

Solubility of Cellulose Triacetate

	+20°	−50°
Acetone	−(37)	++(38)
Methyl acetate	−(39)	(+) (40)

The ratios of ether to ethanol in the experiments with cellulose nitrates were varied considerably. Besides the normal mixture of ether to ethanol (2:1) three other

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[1] Highfield, *Trans. Faraday Soc.*, **22**, 57 (1926).

[2] Werner and Engelmann, *Z. angew. Chem.*, **42**, 437 (1929).