Direct Photolysis of Carbonyl Sulfide in Solution. Mechanism of Singlet D and Triplet P Sulfur Atom Formation

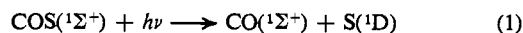## Klaus Gollnick and Eberhard Leppin

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Abstract: COS, photolyzed at 2537 Å and 25° in cyclohexane, cyclopentane, methanol, ethyl alcohol, isopropyl alcohol, and acetonitrile, gives rise to the formation of carbon monoxide and elemental sulfur in all the solvents, but only in alkanes is S insertion into C–H bonds observed. CO and $S(^1D)$ are the primary products which occur with a quantum yield of 0.9 independent of whether the COS photolysis is carried out in alkanes, alcohols, or acetonitrile. Only $S(^1D)$ atoms are capable of C–H insertion reactions; however, they are less reactive in solution than in the gas phase due to a loss of excess translational energy. All solvents catalyze the $S(^3P)$ production from $S(^1D)$ atoms, probably the only pathway by which triplet P sulfur atoms are generated. S_2 formation, the first step in elemental sulfur production, takes place solely by $S(^3P)$ recombination. Whereas reactions of $S(^1D)$ and $S(^3P)$ atoms with COS to give CO and S_2 are very important in the gas phase, no such processes are observed in solutions which contain COS up to 0.7 M.

Photolysis of carbonyl sulfide, COS, and reactions of singlet D and triplet P sulfur atoms, $S(^1D)$ and $S(^3P)$, thus produced have been studied extensively in the gas phase for the past seven years.[1,2] Gas-phase data for the sulfur atom reactions revealed marked similarities among the reactions and chemical reactivities of the group VI atoms (oxygen, sulfur, and selenium) and, moreover, in the chemical behavior of group VI atoms and other divalently unsaturated species such as methylenes (carbenes) and nitrenes.[3]

Whereas liquid-phase data of carbene and nitrene reactions are available, rather limited information exists on sulfur atom reactions in solution.[4,5] Investigations on sulfur atom reactions in the liquid phase seemed, therefore, desirable. Establishing comparative data would allow comparison of the liquid-phase behavior of carbenes, nitrenes, and sulfur atoms and should contribute to an understanding of solvent effects on the chemical reactivities of divalent atoms.[6]

Carbonyl sulfide is probably the most useful source of sulfur atoms because the inert by-product of the COS photolysis, carbon monoxide, permits the monitoring of sulfur atom reactions but avoids the difficulties encountered recently with other sulfur atom sources such as isothiocyanates[4] and thiocyanate ion.[5] However, although it has convincingly been demonstrated that the gas-phase photolysis of COS proceeds according to

$$COS(^1\Sigma^+) + h\nu \longrightarrow CO(^1\Sigma^+) + S(^1D) \qquad (1)$$

the nature of the sulfur atoms produced in the photolysis of COS in the condensed phase remained uncertain.[8,9]

Therefore, a study of the gas- and liquid-phase spectra of COS was recently carried out in order to obtain some information about the primary processes in electronically excited carbonyl sulfide.[10] The present paper deals with the determination of CO quantum yields of liquid-phase COS photolyses in various organic solvents and with the nature and reactions of the sulfur atoms produced.

Experimental Section

COS was purchased from Matheson Company. The impurities, CO_2 and traces of CS_2 and H_2S, were removed by applying the procedure described by Wiebe, *et al.*[11] The purity of COS was controlled gas chromatographically and spectroscopically (by the absence of the strong discrete $\tilde{A}^1B_2 \leftarrow \tilde{X}^1\Sigma_g^+$ system of CS_2 at the short wavelength part of the COS uv absorption spectrum).[10]

Hydrocarbons were Phillips Petroleum Company pure grade and Fluka Purum. Purification was achieved by distillation and running the hydrocarbons through columns of basic Al_2O_3 (Woelm, activity I) before using them in order to get maximum transmission at the wavelength of COS photolysis. Methanol, ethyl alcohol, and acetonitrile (Merck, Uvasol) were used without further purification.

A Rayonet Srinivasan–Griffin reactor (Southern New England Ultraviolet Company) equipped with 16 2537-Å mercury low-pressure Vycor lamps was used for irradiating solutions at 25° in 20- or 150-ml cylindrical quartz vessels. Oxygen was removed by conventional freeze–pump–thaw procedures at 77°K on a mercury-free vacuum system after the solutions were saturated with COS. Care was taken not to irradiate the gas phase by masking it in an appropriate manner.

COS concentrations of saturated solutions were determined gas chromatographically by comparing COS peak areas generated by measured samples of the solutions with those obtained by known amounts of gaseous COS.

After irradiation, the samples were frozen to liquid nitrogen temperature and the noncondensable gases were pumped off by a Toepler pump and measured in a McLeod gauge. Thawing and refreezing were repeated until no noncondensable gas was measured. The composition of the noncondensable gases was determined by gas chromatography (molecular sieve, 5 Å).

The condensable fraction was analyzed by vpc using Perkin-Elmer fractometers F-6 and F-20 (Bodenseewerk) and capillary columns 1-G-26 (50 m, phenylsilicone oil DC550) and 1-G-50

(1) H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **4,** 143 (1966).

(2) O. P. Strausz in "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience Publishers, New York, N. Y., 1967, Chapter 2.

(3) O. P. Strausz and H. E. Gunning in "The Chemistry of Sulfides," A. V. Tobolsky, Ed., Interscience Publishers, New York, N. Y., 1968, Part I, p 23.

(4) U. Schmidt, K. Kabitzke, I. Boie, and C. Osterroth, *Chem. Ber.*, **98,** 3819 (1965).

(5) M. Luria and A. Treinin, *J. Phys. Chem.*, **72,** 305 (1968).

(6) A preliminary note on the chemical behavior of triplet P sulfur and triplet P oxygen atoms toward olefins in the liquid and gaseous phase has appeared.[7]

(7) E. Leppin and K. Gollnick, *Tetrahedron Lett.*, 3819 (1969).

(8) (a) D. A. Stiles, R. Kewley, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.*, **43,** 2442 (1965); (b) H. E. Gunning in "Elemental

Sulfur," B. Meyer, Ed., Interscience Publishers, New York, N. Y., 1965, Chapter 14.

(9) K. S. Sidhu, I. G. Csizmadia, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **88,** 2412 (1966).

(10) E. Leppin and K. Gollnick, *Mol. Photochem.*, in press.

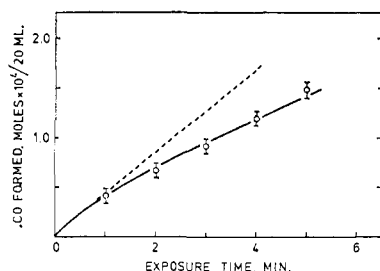(11) H. A. Wiebe, A. R. Knight, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **87,** 1443 (1965).

Figure 1. Formation of carbon monoxide as a function of exposure time.

Figure 2. Formation of cyclohexanethiol vs. formation of carbon monoxide.

(50 m, di-n-decyl phthalate + trimer acid). Because of the small conversions during one run ($\leq 0.5\%$ of the starting amounts of COS) and the resulting minute amounts of reaction products, the starting material was removed by low-temperature distillation before analyzing the condensable products. Qualitative determination was achieved by comparing retention times of the products with those of authentic samples. For quantitative determinations, the method of internal standards was employed after calibration of the detector of the vpc apparatus.

For quantum yield determinations, actinometry was performed at 25° using the uranyl oxalate actinometer. The amount of oxalate decomposition was measured by titration of undecomposed oxalate with potassium permanganate as well as by determination of the amount of CO developed during the oxalate photolysis.[12] In addition, the gas-phase acetone actinometer (at 50 Torr acetone pressure and 125°)[13] was applied. Using Suprasil cuvettes on an optical bench, gas-phase acetone and liquid-phase COS photolyses were performed with conversions less than 0.1%. No filter effect of the elemental sulfur produced in liquid-phase COS photolysis is encountered at such small conversions.

The extinction coefficient of COS at 2537 Å and 25° was determined for the gas and liquid phases by using a Bausch and Lomb 505 uv spectrometer.

Results

In the gas phase and in the organic solvents of Table I, the absorption coefficient of carbonyl sulfide at 2537 Å and 25° was found to be ϵ 2.5 $\pm$ 0.2 l. mol^{-1} cm^{-1}, independent of the applied pressure or concentration of COS. The solubility of carbonyl sulfide in various solvents at 25° and 1 atm of COS is given in Table I.

Table I. Solubility of Carbonyl Sulfide in Organic Solvents at 25° and 1 Atm of COS

Solvent	[COS]$_s$, M	Solvent	[COS]$_s$, M
Cyclohexane	0.684	Acetonitrile	0.376
Cyclopentane	0.474	Benzene	0.771
Methanol	0.378	Toluene	0.730
Ethyl alcohol	0.376	p-Xylene	0.685

(a) Cyclohexane and Cyclopentane

Carbon monoxide, elemental sulfur, and the corresponding mercaptan (cyclohexanethiol or cyclopentanethiol, respectively) are the only reaction products when saturated solutions of COS are irradiated at 2537 Å and 25° in low-conversion runs where less than 0.5% of the initial amount of COS is photolyzed. No other products, in particular no hydrogen sulfide, could be detected.

However, prolonged irradiation results in the formation of sulfides and disulfides by secondary

(12) D. H. Volman and J. R. Seed, J. Amer. Chem. Soc., 86, 5095 (1964).

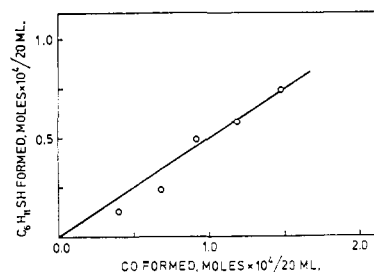(13) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 782.

photolytic decomposition of the primarily formed mercaptans, as was checked by photolyzing cyclohexanethiol in cyclohexane at concentrations corresponding to those obtained in the low-conversion photolyses of COS in cyclohexane.

(b) Methanol, Ethyl Alcohol, Isopropyl Alcohol, and Acetonitrile

Photolysis of saturated solutions of COS at 2537 Å and 25° using alcohols and acetonitrile as solvents yielded carbon monoxide and elemental sulfur as the only reaction products. Mercapto alcohols from ethyl and isopropyl alcohol could not be detected and there was no indication that products of hydrogen abstraction reactions, such as hydrogen sulfide and formaldehyde from methanol, acetaldehyde from ethyl alcohol, or acetone from isopropyl alcohol, were formed.

(c) Quantum Yields of Carbon Monoxide Formation

Figure 1 shows a plot of carbon monoxide developed during photolysis of COS in cyclohexane vs. irradiation periods up to 5 min. The rate of CO formation decreases with the proceeding photolysis of COS due to the filter effect of the dissolved elemental sulfur (ϵ_{2537} 800 per S–S bond[14]) produced. Individual experimental points deviate from the mean values shown in Figure 1 by less than $\pm 5\%$. For quantum yield determinations, initial rates of CO formation were obtained by applying the tangential method. Using the uranyl oxalate actinometry, the quantum yield of CO formation was found to be $\Phi(CO) = 0.90 \pm 0.05$, independent of the COS concentration in the concentration range from 0.082 to 0.684 M studied. The same result was obtained from independent quantum-yield determinations using the photolysis of gaseous acetone at 50 Torr and 125° for actinometry,[13] and photolyzing COS to an extent of less than 0.1% of its initial concentration where filter effects of the sulfur thus produced are negligible.

Figure 2 shows that the yield of cyclohexanethiol increases linearly with the amount of CO formed. Deviations from linearity seem to occur after very short periods of COS irradiation. However, after such short irradiation periods, the amounts of mercaptans to be measured are so small that relatively large errors are expected to appear. Therefore, the more reliable data are those determined after longer irradiation periods. According to Figure 2, the quantum yield of cyclohexanethiol formation equals

(14) H. P. Koch, J. Chem. Soc., 394 (1949).

Table II. CO Quantum Yields of COS Photolysis in Various Solvents at 2537 Å and 25°

Solvents	Viscosity, η^{25}, cP	Light absorption, $\%^a$	CO formation, Torr ml[b] Obsd	Cor[c]	Initial CO quantum yields, $\Phi(CO)$
Cyclohexane	0.980	100	1700	1700	0.90 ± 0.05
Cyclopentane	0.459	94.4	1600	1700	0.90
Acetonitrile	0.345	93.5	1350	1450	$(0.77)^d$ 0.89
Methanol	0.593	82.5	1250	1520	$(0.80)^d$ 0.92
Ethyl alcohol	1.192	77.5	1200	1550	$(0.82)^d$ 0.95

^{a} By COS at 2537 Å under the experimental conditions used. ^{b} After 3 min of irradiation. ^{c} Corrected for light absorption by COS. ^{d} Without accounting for the sulfur filter effect.

$^1/_2\Phi(CO)$ and, consequently, equals the quantum yield of elemental sulfur production.

Quantum yields of CO formation in other solvents are summarized in Table II. They were determined from the amounts of CO formed after 3 min of irradiation and by using the COS photolysis in cyclohexane as a secondary actinometer. In case of the alcoholic solvents and acetonitrile, corrected initial CO quantum yields were obtained by accounting for the fact that in these solvents twice as much elemental sulfur is produced per unit time as in cyclohexane.[15]

Within the limits of error (±0.05), the quantum yield of carbon monoxide production during the photolysis of COS is thus $\Phi(CO) = 0.90$, independent of the nature of the solvent, of the polarities and viscosities of the solvents, and of the COS concentrations used (from about 0.08 to 0.7 M).
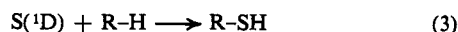
Discussion

As may be inferred from the COS absorption spectra in the gaseous and liquid phase,[10] solvent effects on the carbonyl sulfide molecules are negligible. Thus, absorption of light takes place solely by COS molecules; ground-state COS–solvent complexes are not involved.

Complexes of electronically excited COS with solvent molecules are also not involved in the chemistry which follows the absorption of light since $\Phi(CO)$ is independent of the polarity and viscosity of the solvents used. Furthermore, since $\Phi(CO)$ is the same in mercaptan-forming solvents and in those which do not yield any sulfur-containing products, an "excited molecule mechanism" according to

$$COS^* + R\text{-}H \longrightarrow CO + R\text{-}SH \tag{2}$$
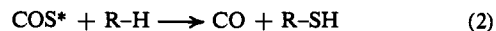
for the mercaptan formation is excluded.

For gas-phase reactions, it has been shown unequivocally that triplet P sulfur atoms, $S(^3P)$, do not react with C–H bonds to give mercaptans.[1-3] There is no reason then to expect $S(^3P)$ atoms to insert into C–H bonds in liquid-phase reactions. That the triplet sulfur atoms are indeed incapable of such a reaction will be shown in forthcoming papers.[16,17] Thus, we conclude that mercaptans are formed exclusively by $S(^1D)$ reactions with C–H bonds

$$S(^1D) + R\text{-}H \longrightarrow R\text{-}SH \tag{3}$$

as is the case in gas-phase reactions,[1-3] and that consequently the primary process of electronically excited COS is its dissociation into CO and $S(^1D)$ atoms. This is supported by the fact that $\Phi(CO)$ in liquid-phase photolyses equals the primary quantum yield of COS dissociation in the gas phase.

Since the absorption of light leads to a stable excited state of COS, from which predissociation occurs into a repulsive state,[10] reaction 1 may be rewritten as

$$COS(^1\Sigma^+) \underset{h\nu}{\rightleftharpoons} {}^1COS^*(^1\Delta \text{ or } {}^1\Sigma^-, \text{ stable}) \longrightarrow$$
$${}^1COS^*(^1\Pi, \text{ dissociative}) \longrightarrow CO(^1\Sigma^+) + S(^1D) \tag{1a}$$

Here, we have accounted for the fact that about 10% of the electronically excited COS molecules return to ground-state COS molecules by nonradiative pathways.[10] Obviously, whence the $S(^1D)$ atoms are formed, no back-reaction with CO to COS occurs in the solvent cage, as can be seen from the fact that $\Phi(CO)$ is independent of the viscosities of the solvents applied.

In contrast to the gas-phase photolysis, reactions

$$S(^1D) + COS \longrightarrow CO + S_2 \tag{4}$$

and

$$S(^3P) + COS \longrightarrow CO + S_2 \tag{5}$$
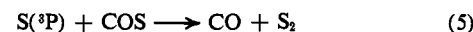
do not seem to play a role in liquid-phase COS photolyses since, up to concentrations of 0.7 M, $\Phi(CO)$ is independent of [COS]. Therefore, S_2 formation (the first step in elemental sulfur production from S_2 units[1]) can only occur by

$$2S(^3P) \longrightarrow S_2 \tag{6}$$

a process which is negligible in the gas phase[1-3] but which may easily take place in the liquid phase, where a third body, necessary for reaction 6 to proceed, is always present.

The obvious reason for reaction 4 not to occur is that, because of the low COS concentration as compared to those of the alkanes, COS cannot compete with alkanes for $S(^1D)$ atoms.[18] The fact that reaction 5 cannot compete with reaction 6 may be accounted for by assuming that an activation energy of at least 10 kcal/mol is associated with reaction 5, whereas reaction 6 proceeds without any activation energy.[19]
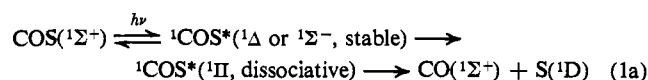
(15) Thus, the sulfur filter effect exerted in alcohols and acetonitrile after 3 min of irradiation should correspond to that exerted in cyclohexane after 6 min of irradiation. Since in cyclohexane the amounts of CO formed after 3 and 6 min of irradiation are 75 and 65% of the theoretical value (see Figure 1), respectively, $\Phi(CO)$ calculated from the corrected CO formation has to be multiplied by $^{75}/_{65}$ in order to obtain initial CO quantum yields for the alcoholic solutions and acetonitrile solution.

(16) E. Leppin and K. Gollnick, *J. Amer. Chem. Soc.*, 92, 2221 (1970).

(17) E. Leppin and K. Gollnick, publication in preparation.

(18) If one makes the reasonable assumption (cf. ref 16) that the rate constant derived for process 3 in the gas phase,[3] $k_3 = 5 \times 10^7$ M^{-1} sec^{-1}, is applicable to liquid-phase reactions, the stationary state concentration of $S(^1D)$ is estimated to be 0.3 $\times$ 10^{-13} M (using the rate of $S(^1D)$ production, 1.4 $\times$ 10^{-5} M sec^{-1} (see Figure 1) and a cyclohexane concentration of 9.3 M). This excludes, of course, S_2 production from $S(^1D)$ dimerization reactions.

(19) In cyclohexane, $2k_6[S(^3P)]^2 = 1.4 \times 10^{-5}$ M sec^{-1} (see Figures 1 and 2). If reaction 6 occurs at a diffusion-controlled rate, i.e., $k_6 \approx 10^{10}$ M^{-1} sec^{-1}, the stationary state concentration of (S^3P) atoms equals 2.7 $\times$ 10^{-8} M. For the given limits of error of ±5% for the $\Phi(CO)$

How are S(^{3}P) atoms, whose existence was proved by trapping them with olefins as episulfides,[17] generated in solution? They could be produced *via* the excited triplet state of COS with a quantum yield of 0.45 in cyclohexane and of 0.9 in alcohols and acetonitrile. This, however, is very unlikely as can be deduced from the potential energy curve diagram of COS.[10] Furthermore, at least part of the sulfur atoms produced in alcoholic solutions and in acetonitrile are S(^{1}D) atoms because they can be trapped by alkanes which, according to reaction 3, gives rise to the formation of mercaptans.[16] Thus, when alkanes are absent in alcoholic solutions and in acetonitrile, the primarily formed S(^{1}D) atoms must undergo transitions to S(^{3}P) atoms. Since this process is strongly spin-forbidden for the free atoms, the solvent molecules obviously "catalyze" this process, probably by charge-transfer interactions.[16]

Although we cannot exclude the possibility that a fraction of the S(^{3}P) atoms may be produced *via* excited triplet COS, we prefer to treat our data by assuming that *all* triplet sulfur atoms formed in direct (*i.e.*, unsensitized) photolysis of COS are generated from S(^{1}D) atoms by solvent-catalyzed processes.
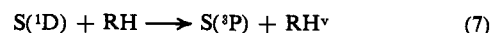
With cyclohexane, this process, generally described

by

$$S(^1D) + RH \longrightarrow S(^3P) + RH^v \qquad (7)$$

(where RH^v = vibrationally excited ground-state solvent molecules), occurs with the same quantum yield as the mercaptan-forming insertion reaction 3; *i.e.*, $k_7/k_3 = 1.0$, whereas this ratio is 0.74 in case of cyclopentane.

This ratio is generally lower in gas-phase reactions and was shown to be dependent on the wavelength of the photolyzing light.[1] Thus, while with λ_{exc} 2537 Å, k_7/k_3 was found to be in the range from 0.50 (cyclopentane) to 0.70 (various other alkanes), this ratio decreases if COS is photolyzed at 2288 Å (Cd-resonance lamp), indicating that the excess translational energy of S(^{1}D) atoms favors the insertion reaction over the deactivation process 7. If COS is photolyzed at 2537 Å, excitation into a higher vibrational level of the stable, electronically excited singlet state of COS, ^{1}COS*($^1\Delta$ or $^1\Sigma^-$, stable), occurs.[10] In the gas phase, dissociation of these excited molecules leads to S(^{1}D) atoms which possess about 6 kcal/mol of excess translational energy.[1-3] In the liquid phase, however, the excited molecules may be deactivated vibrationally to the zero vibrational level of ^{1}COS*($^1\Delta$ or $^1\Sigma^-$, stable) before predissociation takes place, thus leaving less excess translational energy to the S(^{1}D) atoms. S(^{1}D) atoms generated in the liquid phase may, therefore, be expected to be less reactive but more selective in their insertion reactions into the various C-H bonds of alkanes than S(^{1}D) atoms produced in the gas phase. Among others, the following paper will deal with this aspect of singlet D sulfur atom reactions in solution.[16]

determination, k_5[S(^{3}P)][COS] has to be at least 1.4 × 10^{-6} *M* sec^{-1}, *i.e.*, 10% of the value for S$_2$ production in reaction 6, if reaction 5 is to be observable in addition to reaction 6. If one furthermore assumes that reaction 5 is associated with an activation entropy of about −10 to −20 eu, as is generally found for similar reactions,[20] the activation energy at 25° is calculated to be 12 or 9 kcal/mol, respectively. This seems to be a reasonable value since, for reactions such as O(^{3}P) + N$_2$O → N$_2$ + O$_2$[21] and similar ones,[22] activation energies between 20 and 30 kcal/mol were obtained.

(20) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co.,Inc., New York, N. Y., 1941.

(21) F. Kaufmann in "Progress in Reaction Kinetics," Vol. I, G. Porter, Ed., Pergamon Press, Oxford, England, 1961, p 1.

(22) A. F. Trotman-Dickenson in "Advances in Free Radical Chemistry," Vol. I, G. H. Williams, Ed., Logos Press–Academic Press, London, 1965, p 1.