weaker bands. The wavelengths are good to ±1 mμ, the extinctions to ±2%.

Solvents were commercial spectrograde materials. Normal chloroform was freed from ethanol by passing it through a column of neutral alumina. This procedure was also used to purify the $CDCl_3$ and CCl_4 used for pmr spectroscopy. Absolute ethanol for pmr use was dried with Linde molecular sieve until a sample indicated a distinct triplet for the hydroxyl resonance in the pmr spectrum.

Compounds were synthesized (unless otherwise noted) by mixing the β-diketone, etc., with aniline and warming to 80–90° for a brief period. The materials were recrystallized several times. Their properties agreed with the literature values.[24]

2-(N-Phenylacetimidoyl)-1-naphthol, not having been previously reported, was prepared by heating, under nitrogen, 1-hydroxy-2-acetonaphthone and aniline at $\sim$160° for 36 hr. The mass was fractionally sublimed and then recrystallized from benzene-hexane and resublimed, 119.9–120.4°.

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.72; H, 5.79; N, 5.44.

2-(N-Phenylacetimidoyl)phenol was prepared in a similar manner.[24c]

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(24) (a) H. Schiff, *Ann.*, **150**, 193 (1869); (b) C. Beyer, *Ber.*, **20**, 1769 (1887); (c) E. B. Knott, *J. Chem. Soc.*, 977 (1947); (d) S. G. P. Plant and C. R. Worthing, *ibid.*, 1278 (1955); (e) C. M. Chopra and B. H. Iyer, *Current Sci.* (India), **22**, 206 (1953).

The Reactions of Sulfur Atoms. VII. The Ultraviolet Spectrum, the Photolysis, and the Mercury Sensitization of Carbonyl Sulfide

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Received November 15, 1965

Abstract: Ultrapure gaseous COS exhibits a broad absorption continuum in the near-ultraviolet region which starts at 2550 A and extends to below 2000 A with a rounded maximum at 2225 A. Semiempirical molecular orbital calculations, with the inclusion of the sulfur d orbitals, indicate this continuum to correspond to a $\pi \rightarrow \pi^*$ transition since the lowest lying $n \rightarrow \pi^*$ type state appears at considerably higher energies. Photolysis in this region affords CO (Φ = 1.81 at 2537 and 2288 A) and sulfur. The primary step yields S atoms at least 74% of which are formed in the excited (^1D) state. The mercury photosensitization at 2537 A affords only triplet-ground-state sulfur atoms. Both singlet- and triplet-state atoms abstractively attack COS to form S_2 with the rate ratio, $S(^1D)/S(^3P)$, being *ca.* 30. The condensed-phase photolysis is similar to that of the gas phase although the relative yields of triplet- and singlet-state atoms may be altered.

Over 30 years ago it was suggested on energetic grounds that the photolysis of gaseous COS in its first absorption continuum results in carbon monoxide and $S(^1D)$ atoms.[2] This postulate has been proven, however, only in recent years by trapping the atomic sulfur with hydrocarbons.[3–6] When the photolysis is carried out in the presence of an olefin or paraffin, episulfide and/or mercaptan form, respectively, in high yields. The alkyl mercaptan has been shown to arise without the intervention of free radicals, by an insertion-type mechanism, which is possible only if the S atoms produced in the primary photolytic step are in their excited singlet D state, 26.4 kcal/mole above the triplet P_2 ground level.[7] It has also been demonstrated that the insertion reaction can be effectively suppressed by collisional relaxation of the $S(^1D)$ atoms to the ground state.

In the early study of Forbes and Cline,[8] the quantum yield of CO was reported to be nearly unity. Later Kondratjev,[9] from the photooxidation of COS, concluded that S atoms attack COS, to form S_2 and CO. We reported[3,5,6] recently that Φ(CO) decreases with increasing olefin pressure to a limiting value of exactly one-half of that in the absence of olefin. Therefore the abstraction reaction at room temperature and over 50 torr of COS must go to completion. Consequently Φ(CO) for pure COS should be 2 unless the photodecomposition is inherently inefficient.

The ultraviolet absorption spectrum of COS has been reported to possess two continua,[10] with the lower energy continuum extending with maxima at 2080 and 2250 A, from 2550 down to *ca.* 1600 A. At very low pressures the first continuum was reported to resolve into several broad, diffuse bands involving a number of different electronic transitions thought to arise from an $n \rightarrow \pi^*$ type excitation. The second absorption region sets in at *ca.* 1550 A.

The spectrum has been discussed by Walsh,[11] and relevant information may be found in one of Mulliken's

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(1) (a) University of Alberta; (b) University of Toronto.

(2) W. Lochte-Holtgreven, C. E. H. Bawn, and E. Eastwood, *Nature*, **129**, 869 (1932).

(3) (a) O. P. Strausz and H. E. Gunning, *J. Am. Chem. Soc.*, **84**, 4080 (1962); (b) A. R. Knight, O. P. Strausz, and H. E. Gunning, *ibid.*, **85**, 1207, 2349 (1963).

(4) A. R. Knight, O. P. Strausz, S. M. Malm, and H. E. Gunning, *ibid.*, **86**, 4243 (1964).

(5) H. A. Wiebe, A. R. Knight, O. P. Strausz, and H. E. Gunning, *ibid.*, **87**, 1443 (1965).

(6) K. S. Sidhu, E. M. Lown, O. P. Strausz, and H. E. Gunning, *ibid.*, in press.

(7) National Bureau of Standards, Circular 467, U. S. Government Printing Office, Washington, D. C., June 15, 1949.

(8) G. S. Forbes and J. E. Cline, *J. Am. Chem. Soc.*, **61**, 151 (1939).

(9) A. Kondratjev and A. Yakovleva, *Russ. J. Phys. Chem.*, **14**, 853 (1940).

(10) W. C. Price and D. M. Simpson, *Proc. Roy. Soc.* (London), **A169**, 501 (1939).

(11) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

more recent articles.[12] Important contributions to the interpretation of the spectrum came from the only quantum mechanical study on COS reported by Clementi[13] in 1963 in the LCAO–MO–SCF framework using Slater-type orbitals (STO) as basic functions. He sought an answer to the question whether the closed L shell in sulfur is just as inert (*i.e.*, separated from the valence M shell) as the K shell in carbon and oxygen. The conclusion "from the orbital energies as well as from the coefficients" is that the 2s, $3p_\sigma$, and $2p_\pi$ orbitals (of the sulfur) are "certainly to be considered atomic in character with very slight core-valency electron polarization."

Additional implications of Clementi's calculations are: (a) the MO levels obtained indicate that the type of the first excited state is π–π^*. The nearest σ–π^* and π–σ^* states are energetically quite close to each other but considerably higher than the first excited state, and (b) the result that the K shells of C, O, S are perfectly independent and the L shell of the S atom is almost completely detached from the valence electrons justifies the use of semiempirical calculations on COS, treating the valence electrons only.

Since only s- and p-type atomic orbitals (AO's) were used in the calculations no information is available on the effect of the empty 3d orbitals of sulfur on the various excited states.

Since the photolysis of COS is a very important source of atomic sulfur for kinetic-mechanistic investigations, a detailed study appeared justified to correlate the spectrum and the type of excited states with the primary photochemical step. For this reason we have (a) reexamined the ultraviolet spectrum, (b) studied the photolytic and triplet mercury-sensitized decomposition of COS, including the effect of phase shift on the photolysis, and (c) carried out an MO calculation on the molecule.

Experimental Section

The absorption spectrum of ultrapure COS was measured in a 10-cm long quartz cell by Cary, Model 14M, and Perkin-Elmer, Model 350, spectrophotometers at 26 ± 1°. The COS purification procedure was described earlier.[5]

In the photolysis study at 2537 A, a mercury-free vacuum system was used. The irradiation source was a Hanovia low-pressure mercury resonance lamp with a Vycor 7910 filter. The cylindrical photolysis cell was 60 mm in length and 50 mm in diameter. It was cleaned before each experiment. The intensity of the roughly collimated 2537-A beam was monitored by a CBS Laboratories Type CL-1010 phototube equipped with a 2537-A interference filter, which was placed behind the photolysis cell. HBr actinometry was used to calibrate the phototube and the incident intensities (7.79×10^{14} quanta/sec) were also measured by mercury-propane actinometry.

In the 2288-A photolysis the source was an unfiltered Osram Cd resonance lamp and HBr was used for actinometry.

The time of irradiation was adjusted at each pressure of COS to give approximately 2 μmoles of CO. In every experiment the transmitted intensity decreased with time due to deposition of sulfur on the cell faces. Suitable corrections were made for this effect. At the conclusion of irradiation, CO was removed at −196° and measured in a gas buret.

In the mercury photosensitizations the decomposition was kept low with the CO produced being between 0.4 and 0.6 μmole. No significant mercury depletion occurred under these conditions.

In the condensed phase experiments, irradiation was effected in small vacuum-sealed quartz ampoules or in cylindrical cells with plane parallel quartz windows, immersed in liquid nitrogen.

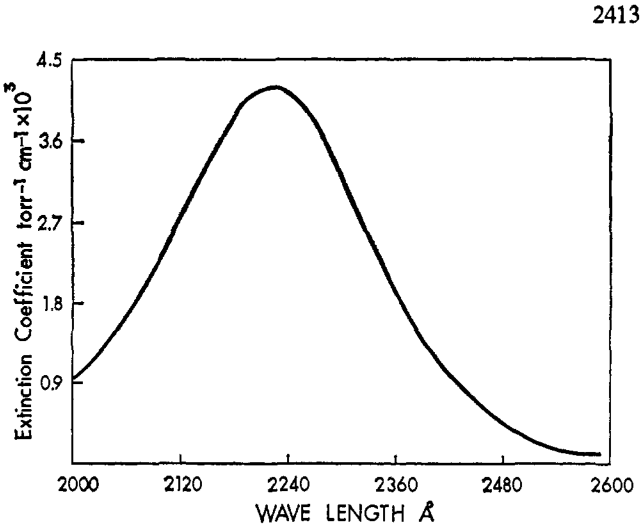

Figure 1. Absorption coefficient of COS as a function of wavelength.

Results and Discussion

The absorption coefficient of gaseous COS in the 2600- to 2000-A region and at 14–112 torr pressure is plotted against wavelength in Figure 1. The short wavelength half of this spectrum is entirely different from that reported by Forbes and Cline.[8] We conclude that their sample was impure. Price and Simpson[10] reported a break in the spectrum around 1600-A. Extrapolation of our curve would show fadeout around 1800 A.

The radiative lifetime of the initially formed upper state can be estimated from the relation[14]

$$\tau = \frac{3.381 \times 10^{10}}{\Pi^4 \int \epsilon d\nu \times \nu^2}$$

where ϵ is the absorption coefficient and ν is the average wavenumber, in cm^{-1}, of the absorption band. The radiative lifetime is estimated to be 10^{-9} sec.

Photolysis. The quantum yield of carbon monoxide formation is independent of pressure between 80 and 680 torr, and from six measurements (at λ = 2537 A) the value is 1.81. Since the rate of CO formation has been shown to be suppressible by olefins to a limiting value exactly half of that for pure COS, it follows that the quantum yield of the primary step

$$\text{COS} + h\nu \longrightarrow \text{COS}^* \longrightarrow \text{CO} + \text{S} \tag{1}$$

is equal to 0.91. The slight inefficiency may be due to experimental error, or to radiative or nonradiative transitions to the ground state. The quantum yield of CO formation at 2288 A, from several experiments, was found to be approximately 1.8 from which Φ(primary) = 0.90. Thus the lifetime of the excited COS with respect to decomposition should be $\leqslant 10^{-10}$ sec.

The alternate possible step

$$\text{COS}^* + \text{COS} \longrightarrow 2\text{CO} + \text{S}_2$$

can be neglected for the reasons that it could not explain the insertion reactions of atomic sulfur from the photolysis of COS in paraffin C–H bonds,[3,4] and also the addition of inert gases to COS undergoing photolysis has little or no effect on the CO (or other products) yields.[3,5,6]

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(12) R. S. Mulliken, *Can. J. Chem.*, **36**, 10 (1958).

(13) E. Clementi, *J. Chem. Phys.*, **36**, 750 (1962).

(14) J. N. Murrell, "The Theory of Electronic Spectra of Organic Molecules," John Wiley and Sons Inc., New York, N. Y., 1963, p 8.

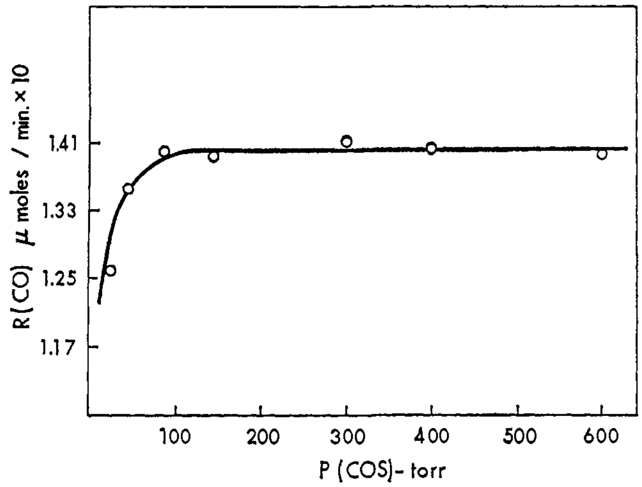

Figure 2. Rate of CO formation as a function of COS pressure from the mercury photosensitization of COS.

From data[3,4] derived from S-atom + paraffin reactions, 74% of the sulfur atoms produced in (1) could be scavenged by insertion into paraffinic C–H bonds, therefore

$$COS(^1\Sigma^+) + h\nu \longrightarrow CO(^1\Sigma^+) + S(^1D) \quad \Phi_{min} = 0.67 \quad (2a)$$

$$\longrightarrow CO(^1\Sigma^+) + S(^3P) \quad \Phi_{max} = 0.24 \quad (2b)$$

Taking $\Delta H_f(S_g)^{15} = 66.0$, $\Delta H_f(COS)^{16} = -32.8$, and $\Delta H_f(CO)^{16} = 26.4$ kcal/mole, step 2a becomes energetically possible at 72.4 + 26.4 = 98.8 kcal/mole, corresponding to λ 2895 A.

On the same basis to produce S atoms in the next lowest lying $^1S_0$ state by

$$COS(^1\Sigma^+) + h\nu \longrightarrow CO(^1\Sigma^+) + S(^1S_0) \quad (3)$$

the minimum energy would be 135.8 kcal/mole or λ 2105 A.

Steps 2a and 3 are spin allowed. Step 2b, however, is spin forbidden.

Further reactions of importance in the sequence are

$$COS(^1\Sigma^+) + S(^1D) \longrightarrow CO(^1\Sigma^+) + S_2(?) \quad (4a)$$

$$\longrightarrow COS + S(^3P) \quad (4b)$$

$$nS_2 \longrightarrow S_{2n} \quad (5)$$

Step 4a would be spin allowed if S_2 is formed in one of its low-lying excited singlet state. The reaction with thermalized $S(^1D)$ atoms, to produce S_2 in its ground $^3\Sigma_g^-$ state, is exothermic to the extent of 101.5 − 72.4 + 26.4 = 55.5 kcal/mole, while the lowest lying excited singlet states of S_2, *i.e.*, $^1\Delta_g$ and $^1\Sigma_g^+$, are respectively ∼13 and 24 kcal/mole above the ground state.[17] Indications are, from flash photolysis–kinetic spectroscopic studies,[18] that S_2 is not produced in its ground electronic state.

Step 4b has been shown to have minor significance,[6] and the relative efficiency of 4b, as compared to abstraction *via* (4a), is ∼0.13.

The polymerization reaction, step 5, is complex. At high COS pressures presumably only the even-number species, S_2, S_4, S_6, and S_8, are present. At low pressures (0.2 torr), however, all species from S_2 to S_8 (but not higher) were detected by flash photolysis–kinetic mass spectrometry.[19]

While Φ(CO) is independent of COS pressure, inert gases slightly decrease CO formation, probably through the recombination reaction

$$S + S + M \longrightarrow S_2 + M \quad (6)$$

Hg($^3P_1$)-Sensitized Photolysis. Rates of CO formation against COS pressure are plotted in Figure 2. A steady value of 0.14 μmole/min is reached at a COS pressure of *ca.* 80 torr which corresponds to Φ = 1.79. The initial increase is due to increased quenching and absorption by the pressure broadening of the mercury resonance line.

The following reaction sequence may be written.

$$Hg(^3P_1) + COS(^1\Sigma^+) \longrightarrow Hg(^1S_0) + CO(^1\Sigma^+) + S(^3P) \quad (7a)$$

$$\longrightarrow HgS + CO \quad (7b)$$

$$COS + S(^3P) \longrightarrow CO + S_2, \text{etc.} \quad (8)$$

That Φ(CO) is nearly the same as that for direct photolysis indicates that primary step 7b does not occur. The spin conservation principle requires the S atoms to be formed in their ground triplet state. That this is indeed the case was proven by experiments with added propane and 2-butene. In neither case was any mercaptan formed, indicating the absence of $S(^1D)$ atoms, and consequently reaction 7a provides an additional example for the illustration of the spin conservation rule in triplet mercury photosensitization. It should also be noted that this is in spite of the fact that the exothermicity of the reaction would be sufficient to promote S atoms to the ($^1D_2$) state in which case the least amount of electronic energy would be converted into vibrational and kinetic energy.

The abstraction reaction (8) proceeds to completion as with singlet atoms. However, a significant difference in the rate of the reaction is apparent. From measurements of the CO and episulfide yields in the sensitized and direct photolysis of COS in the presence of 2-butene, the following relative rate values were obtained

$$\frac{R(COS + S(^1D))}{R(\text{2-butene} + S(^1D))} \Big/ \frac{R(COS + S(^3P))}{R(\text{2-butene} + S(^3P))} \geqslant \sim 30$$

that is, the relative rate of abstraction from COS to addition to the double bond to form episulfide is about 30 times larger for $S(^1D)$ than $S(^3P)$ atoms. Furthermore, it is reasonable to assume that $S(^1D)$ atoms would not react more slowly with 2-butene than $S(^3P)$ atoms and, therefore, $R(COS + S(^1D))/R(COS + S(^3P)) \geqslant \sim 30$.

Condensed-Phase Photolysis. A liquid solution of COS in ethylene (1:2.8 mole ratio) was irradiated at room temperature with a medium pressure Hanovia lamp through a Vycor 7910 filter. The two sulfur-containing products were vinyl mercaptan and ethylene episulfide in a mole ratio of 0.43:1. In the gas

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(15) T. L. Allen, *J. Chem. Phys.*, **31**, 1039 (1959); L. Brewer, *ibid.*, **31**, 1143 (1959); R. Colin, P. Goldfinger, and M. Juenchromme, *Nature*, **187**, 408 (1960); H. Mackle, *Tetrahedron*, **19**, (1963); T. F. Palmer and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 4661 (1962); J. Berkowitz and J. R. Marquart, *J. Chem. Phys.*, **39**, 275 (1963); H. Mackle, Abstracts of Papers, Sulfur Symposium, Calgary, Alberta, Canada, March 18, 1964; A. N. Singh and D. K. Rai, *J. Chem. Phys.*, **43**, 2151 (1965)

(16) "Selected Values of Thermodynamic Properties," National Bureau of Standards, Circular U. S. Government Printing Office, Washington, D. C., 1952.

(17) R. F. Barrow and R. P. du Parcq, "Elemental Sulfur," B. Meyer, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, Chapter 13.

(18) M. de Sorgo, P. Fowles, A. J. Yarwood, O. P. Strausz, and H. E. Gunning, to be published.

(19) W. K. Duholke, R. P. Messmer, P. Kebarle, O. P. Strausz, and H. E. Gunning, to be published.

phase reaction[5] at a similar ratio of the two reactants (and at a total pressure of *ca.* 400 torr) the corresponding product ratio was 0.90 : 1.00.

The mercaptan, being a characteristic product of singlet-state sulfur atom reactions, seems to indicate that S(^{1}D) atoms are also formed in the liquid phase photolysis of COS. The lower relative yield of the vinyl mercaptan in the condensed phase is due either to a more efficient electronic relaxation of S(^{1}D) atoms to the ground state or more likely to an intersystem crossing in the excited COS to a repulsive triplet state yielding S(^{3}P) atoms.

When a 1 : 10 mole ratio solution of COS in propylene was irradiated in the solid phase at liquid nitrogen temperature, in addition to a minor unidentified product, three isomeric sulfur compounds, namely methyl vinyl mercaptan, allyl mercaptan and propylene episulfide—the principal products of the gas phase reaction—were formed in a relative yield of 0.10 : 0.034 : 1.00, respectively. In the gas phase at similar mole ratios of reactants (and at 900 torr total pressure), the corresponding product ratios were 0.21 : 0.25 : 1.00. Thus S(^{1}D) atoms form in the low-temperature solid phase photolysis as well, but again the relative yields of mercaptans are greatly diminished.

Molecular Orbital Calculations. An "extended Hückel molecular orbital" calculation[20] was carried out for COS with and without the inclusion of 3d atomic orbitals (AO's) of the sulfur atom. In the latter case 12 Slater-type AO's (s, p_x, p_y, and p_z type for each of the three atoms) while in the former case 17 Slater-type orbitals (the same 12 AO's plus a set of five 3d orbitals for S) were used to make up the molecular orbitals (MO's) by linear combination (LCAO–MO).

$$\Phi_i = \sum_{j=1}^{N} C_{ij}\eta_j \qquad i = 1\ldots N \tag{9}$$

In eq 9 Φ_i represents the *i*th MO, η_j represents the *j*th AO, and the value of *N* in this case may be 12 or 17 as described above. The molecular one-electron energy values (MO energies), ϵ_i, as well as the coefficients (*C*) of the linear combination, resulted as the solution of the secular problem

$$\sum_{i=1}^{N} (H_{ij} - \epsilon_i S_{ij})C_{ij} = 0 \qquad j = 1\ldots N \tag{10}$$

The overlap integrals (S_{ij}) were evaluated explicitly, and the off-diagonal elements (H_{ij}) were estimated from the diagonal atomic one-electron energy values (H_{ii}, H_{jj}) according to Hoffman

$$H_{ij} = 1.75\left(\frac{H_{ii} + H_{jj}}{2}\right)S_{ij} \tag{11}$$

The empirical atomic one-electron energy values used in the calculation are shown in Table I, and the corresponding orbital energy values are summarized in Figure 3. The labeling of the molecular orbitals was made to match with that of Clementi for ease of comparison.

It is interesting to see the effect (Figure 3) of the 3d-orbital inclusion. The set of five 3d AO's of sulfur creates five new MO's, one of which is of σ type (10σ*), two π types (5π_x* and 5π_y*), and two δ types (δ_{xy}*). These latter ones are composed entirely of sulfur 3d AO's.

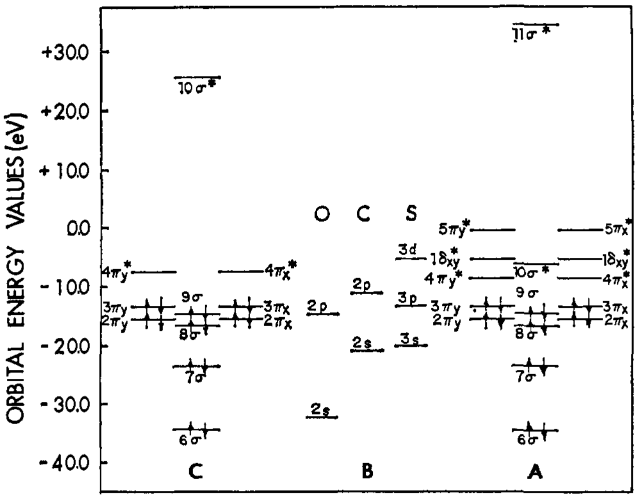

Figure 3. MO energy levels from semiempirical calculations. A and C are with and without the inclusion of the sulfur d orbitals, respectively. B represents the AO energies.

All the five new MO's are empty (antibonding) as indicated by the asterisk. The inclusion of d orbitals does not appreciably affect the energy levels of the filled (bonding) MO's. However, it does affect the originally present antibonding π orbitals (4π_x and 4π_y) by lowering their energy. Consequently it is expected that ground-state properties of the molecule are relatively insensitive to d orbitals, while the description of excited states is affected by the inclusion of d orbitals. This implies, therefore, that the inclusion of 3d orbitals of sulfur is important in the theoretical analysis of experimental ultraviolet spectral studies. The quantitative involvement of sulfur 3d AO's in individual MO's can be seen from the coefficient matrix as shown in Table II.

Table I. Atomic Orbital Energy (H_{ii}) Values (ev) Estimated as Orbital Ionization Potentials and Electron Affinity

	Atom (*n*)[a]		
	C (2)	O (2)	S (3)
d	. . .	. . .	−5.40
p	−11.27	−14.80	−13.80
s	−21.01	−32.30	−20.10

[a] *n* = principal quantum number of the valence shell.

The loosely bonding and weakly antibonding molecular orbitals (Φ_i) are usually considered to be chemically important. Orbital energies (ϵ_i) of these MO's from both Clementi's nonempirical calculation and the present semiempirical approach are tabulated in Table III. The energetically four lowest excitations that one can derive from these chemically important orbitals by taking differences are summarized in Table IV and Figure 4.

No attempt was made to predict relative intensities on the basis of symmetry. Lines, however, that are associated with the promotion of an electron between MO's of like symmetry ($\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$) are arbitrarily drawn (Figure 4) with double height. Each transition,

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(20) R. Hoffman, *J. Chem. Phys.*, 39, 1397 (1963).

Table II. Computed MO Coefficients Including Sulfur 3d AO's in Linear Combination

Atom	AO	Vacant MO's								
		$12\sigma^*$	$11\sigma^*$	$5\pi_x^*$	$5\pi_y^*$	$1\sigma_{xy}$	$1\pi_{xy}$	$10\sigma^*$	$4\pi_x^*$	$4\pi_y^*$
S	3s	1.2524	−0.0133	0.	0.	0.0000	0.	−0.2272	−0.	0.
	$3p_x$	0.	0.	0.3271	0.	−0	0.	−0.	0.4486	0.
	$3p_z$	−1.3495	0.0773	−0.	−0	−0.0000	−0.	0.3484	0.	−0.
	$3p_y$	0.	0.	0.	0.3271	−0.	0.	−0.	−0.	0.4486
	$3d_{x^2-y^2}$	−0.4931	0.1029	−0.	−0.	0.8660	−0.	−0.4418	0	−0.
	$3d_{xz}$	0	0.	−1.0303	0.	−0.	0.	−0.	0.4343	0.
	$3d_{z^2}$	0.8541	−0.1782	0.	0.	0.5000	0.	0.7652	−0.	0.
	$3d_{xy}$	0.	0.	0.	0.	−0.	1.0000	−0.	−0.	0.
	$3d_{yz}$	−0.	−0.	−0.	−1.0303	0.	−0.	0.	0.	0.4343
C	2s	−1.4535	1.1032	−0.	−0.	−0.0000	−0.	0.1673	0.	−0.
	$2p_x$	0.	0.	−0.8596	0.	−0.	0.	−0.	−0.6916	0.
	$2p_z$	−1.4152	−1.0944	−0.	−0.	−0.0000	−0.	0.1814	0.	−0.
	$2p_y$	−0	−0.	−0.	−0.8596	0.	−0.	0.	0.	−0.6916
O	2s	−0.3273	−1.0854	−0.	−0.	0.0000	−0.	−0.1042	0.	−0.
	$2p_x$	0.	0.	0.2532	0.	−0.	0.	−0.	0.4158	0.
	$2p_z$	−0.1628	−0.8285	−0.	−0.	0.0000	−0.	−0.1229	0.	−0.
	$2p_y$	0.	0.	0.	0.2532	−0.	0.	−0.	−0.	0.4158

Atom	AO	Occupied MO's							
		$3\pi_x$	$3\pi_y$	9σ	$2\pi_x$	$2\pi_y$	8σ	7σ	6σ
S	3s	0.	−0.	−0.2898	−0.	0.	0.5129	0.6157	−0.0458
	$3p_x$	0.8404	−0.	−0.	0.2479	0.	−0.	−0.	0.
	$3p_z$	−0.	0.	−0.6151	0.	−0.	0.4172	−0.0742	−0.0052
	$3p_y$	0.	0.8404	−0.	−0.	0.2479	−0.	−0.	0.
	$3d_{x^2-y^2}$	−0.	0.	−0.0150	0.	−0.	0.0096	0.0198	−0.0288
	$3d_{xz}$	0.0027	−0.	−0.	0.0094	0.	−0.	−0.	0.
	$3d_{z^2}$	0.	−0.	0.0259	−0.	0.	−0.0167	−0.0344	0.0499
	$3d_{xy}$	0.	−0.	−0.	−0.	0.	−0.	−0.	0.
	$3d_{yz}$	−0.	0.0027	0.	0.	0.0094	0.	0.	−0.
C	2s	−0	0.	0.0825	0.	−0.	−0.2406	0.3916	−0.3224
	$2p_x$	0.2024	−0.	−0.	0.3823	0.	−0.	−0.	0.
	$2p_z$	−0.	0.	0.2431	0.	−0.	0.0415	0.2352	0.0660
	$2p_y$	−0.	0.2024	0.	0.	0.3823	0.	0.	−0.
O	2s	−0.	0.	0.0637	0.	−0.	0.2188	−0.2786	−0.8055
	$2p_x$	−0.4769	−0.	−0.	0.7775	0.	−0.	−0.	0.
	$2p_z$	−0.	0.	−0.6027	0.	−0.	−0.6228	0.1407	0.0229
	$2p_y$	0.	−0.4769	−0.	−0.	−0.7775	−0.	−0.	0.

except for the $\sigma \rightarrow \sigma^*$ lines, are degenerate owing to the linear geometry of the molecule. Significantly the first transition predicted is a $\pi \rightarrow \pi^*$, while the n → π^* type (labeled as $9\sigma \rightarrow 4\pi^*$) appears at higher energy, but still well within the first absorption band.

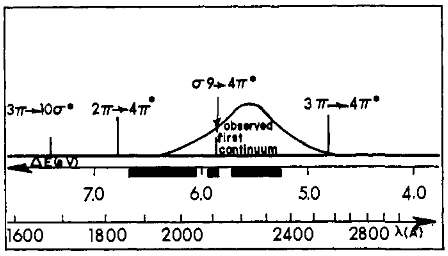

Figure 4. The lowest lying transitions predicted by the semiempirical calculations with d orbital inclusion.

Such semiempirical MO calculations cannot be expected to reproduce the experimental excitation energies (ΔE). It seems reasonable, however, to make a temporary assignment at this stage. It is quite likely that the first observed band at the near ultraviolet (1900 A < λ > 2600 A) includes the $3\pi \rightarrow 4\pi^*$ excitation. As it might be expected, these excited states have different dipole moments from that of the ground state. In order to get some preliminary idea about the charge distributions, Mulliken's population analysis was carried out on the corresponding double excited states. The results are tabulated in Table V. In the course of $\pi \rightarrow \pi^*$ excitation charge is transferred mostly from S toward C, while the effect on the O=C portion of the molecule is relatively small. As the result of the σ

Table III. Chemically Important MO Energies of COS

Orbital	Nonempirical[18] s, p		Semiempirical	
	au	ev	s, p ev	s, p, d ev
$10\sigma^*$	+0.34606	+9.4163	+25.7798	−6.2655
$4\pi^*$	+0.18106	+4.9266	−7.6229	−8.8734
3π	−0.36174	−9.8429	−13.6826	−13.6827
9σ	−0.55066	−14.9835	−14.7315	−14.7401
2π	−0.64355	−17.5110	−15.6722	−15.6731
8σ	−0.72180	−19.6418	−16.6434	−16.6477

Table IV. Estimated Excitation Energies (ev) of the Low-Lying States of COS

Excitation Type	Electron configuration					Non-[13] empirical s, p	Semiempirical s, p	Semiempirical s, p, d
$3\pi \rightarrow 10\sigma^*$	$2\pi^4$	$9\sigma^2$	$3\pi^3$	$4\pi^0$	$10\sigma^1$	20.26	39.46	7.42
$2\pi \rightarrow 4\pi^*$	$2\pi^3$	$9\sigma^2$	$3\pi^4$	$4\pi^1$	$10\sigma^0$	22.44	8.05	6.80
$9\sigma \rightarrow 4\pi^*$	$2\pi^4$	$9\sigma^1$	$3\pi^4$	$4\pi^1$	$10\sigma^0$	19.91	7.11	5.87
$3\pi \rightarrow 4\pi^*$	$2\pi^4$	$9\sigma^2$	$3\pi^3$	$4\pi^1$	$10\sigma^0$	14.77	5.06	4.81
Ground	$2\pi^4$	$9\sigma^2$	$3\pi^4$	$4\pi^0$	$10\sigma^0$	...	...	...

Table V. Approximate Charge Distribution in the Three Lowest Electronic States of COS

Electronic state	Net charges O	C	S
$9\sigma \rightarrow 4\pi^*$	−0.65	+0.85	−0.20
$3\pi \rightarrow 4\pi^*$	−0.83	+0.77	+0.06
Ground	−0.94	+1.18	−0.24

→ π^* excitation, the C=S moiety remains almost unaltered and the charge migrates from O toward C.

The nature of the excited states are complicated by the fact that a given electron configuration may involve several states. This is the result of the fact that these configurations represent double open-shell problems.[21] In the case of linear molecules (like COS) all $\pi \rightarrow \pi^*$ configurations can assume three singlet ($^1\Sigma^-$, $^1\Delta$, $^1\Sigma^+$) and three triplet ($^3\Sigma^-$, $^3\Delta$, $^3\Sigma^+$) states, and $\sigma \rightarrow \pi^*$ as well as $\pi \rightarrow \sigma^*$ configurations may exist in two states of different multiplicity ($^1\Pi$, $^3\Pi$).

By analogy with carbon dioxide[11,12,22] one can assign an energy scheme for the various states. Figure 5 shows a schematic representation of the four lowest excited states associated with the first two electronic configurations above the ground state. The fact that the $^1\Sigma^+$ and $^1\Delta$ states are quite close to each other could mean an easy crossing with the change of molecular geometry. The first allowed transition, however, is $^1\Sigma^+ \rightarrow {}^1\Sigma^+$ according to the selection rule.

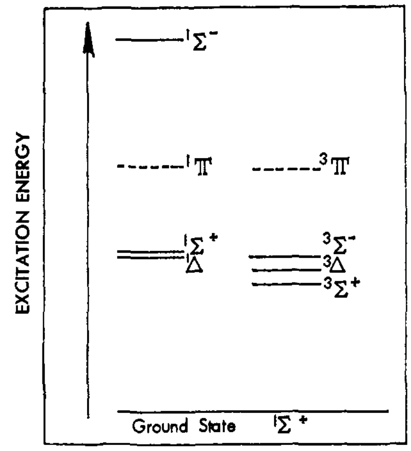

Figure 5. A schematic representation of the electronic states associated with the first two electronic configurations above the ground state.

Some of the excited states are bent. If one assumes that the O=C bond length does not change appreciably upon excitation, then one still faces the problem of studying a potential surface as a function of C–S and O–C–S bending. In accordance with the Franck–Condon principle, the system most likely arrives at these surfaces upon excitation with retention of its linear structure. Hence a section of the potential surface that is a potential curve as a function of C–S distance would be quite satisfactory, to the first approximation, for a detailed understanding of the photolysis. However, no such potential curve is available at the present. We therefore tentatively suggest that the mercury photosensitization proceeds *via* energy transfer from Hg $6(^3P_1)$ to COS, raising it to the repulsive $^3\Sigma^+$ state. The direct photolysis between 2288 and 2550 A may be envisaged *via* the $^1\Sigma^+$ state for which transition from the ground state is allowed. Singlet → triplet intersystem crossing appears to be more important in the condensed phase than in the gas phase.

Further studies on COS are in progress.

Acknowledgment. The authors are indebted to Dr. A. R. Knight for the 2288-A quantum yield measurement, and to Imperial Oil Limited for financial support.

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(21) S. Huzinaga, *Phys. Rev.*, 120, 886 (1960).

(22) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, Inc., New York, N. Y., 1964, p 68.