Sensitized Photolysis of Carbonyl Sulfide in Solution. Photosensitization by Aromatic Hydrocarbons. Products and General Phenomena

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Abstract: COS photolysis in benzene, toluene, and *p*-xylene sensitized by these aromatic hydrocarbons gives rise to the formation of carbon monoxide and sulfur atoms with average quantum yields $\Phi(CO) = \Phi(S) = 0.55$. The sulfur atoms may be trapped by olefins as episulfides. No C–H insertion products from olefins (mercaptans) are observed, in accord with the assumption that all the sulfur atoms reacting are in the triplet P state. Trimethylethylene is appreciably more reactive than cyclohexene. The formation of cyclohexene episulfide occurs with a surprisingly low rate constant of the order of $10^2\ M^{-1}\ sec^{-1}$.

Whereas the gas-phase photolysis of COS at 2537 Å has been extensively used as a source for the production of sulfur atoms in gaseous systems,[1] it was only recently that more detailed investigations of the direct COS photolysis in liquid solution and of reactions of sulfur atoms in liquid solution have been reported.[2,3] Carbon monoxide and singlet D sulfur atoms, $S(^1D)$, were found to be the primary products of the direct COS photolysis at 2537 Å in both the gaseous and the liquid phase. $S(^1D)$ atoms, produced according to[4]

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

may undergo insertion reactions into the C–H bonds of saturated hydrocarbons or deactivation reactions to triplet P sulfur atoms, $S(^3P)$, by collisions with these hydrocarbons.[1–5] In liquid alcohols (methyl, ethyl, and isopropyl alcohols) and acetonitrile, however, only deactivation to $S(^3P)$ takes place.[2] Since $S(^3P)$ atoms are incapable of inserting into C–H bonds[1–3] but are easily trapped by olefins as episulfides,[1,6] direct photolysis of COS in alcohols and acetonitrile might be considered as a convenient source of triplet P sulfur atoms. However, there are some disadvantages connected with such systems: (1) the molar decadic extinction coefficient of COS at 2537 Å is rather small ($\epsilon_{2537} = 2.5 \pm 0.3\ M^{-1}\ cm^{-1}$ [2,4,7,8]) so that conversions have to be kept very low in order to avoid photolytic decomposition of the stronger absorbing reaction products,[9] and (2) photolysis at shorter wavelengths (where COS absorbs more strongly[4,8]) is complicated by the fact that most of the solvents start to absorb the light of this short-wavelength region.

In order to obtain a convenient source of $S(^3P)$ atoms in liquid solution, we had to change from direct photolysis of COS to sensitized COS photolysis in which the sensitizer should fulfill the following conditions: (1) it should strongly absorb at a convenient wavelength; (2) it should show a high population of its triplet state and transfer its electronic excitation energy to COS exclusively and with high efficiency; (3) if singlet–singlet energy transfer takes place, the $S(^1D)$ atoms thus formed should efficiently (if not exclusively) be transformed to $S(^3P)$ atoms. Triplet mercury, $Hg(^3P_1)$, an excellent sensitizer for the photolysis of COS in the gas phase,[1] does not meet these conditions in solution, and triplet carbonyl sensitizers such as benzophenone, acetophenone, xanthone, and dicyclopropyl ketone were found to be unreactive; only acetone showed a slight sensitizing effect.[4] Thus, we started an investigation on aromatic hydrocarbons as sensitizers (and solvents) of the photolytic decomposition of COS. Their triplet energies should exceed the energy of the lowest dissociative triplet state of COS (78–80 kcal/mol[4]), and even though their singlet energies are also high enough to make singlet–singlet energy transfer from the excited aromatic hydrocarbon to COS (E_s(COS) = 106 kcal/mol[4]) possible, the $S(^1D)$ atoms thus formed would be expected to decay rapidly to the ground state in the aromatic hydrocarbon solvent, as has been observed in alcohols and acetonitrile.[2,6] The results of these studies will be presented in this and subsequent communications.

Experimental Section

COS, purchased from Matheson Co., contained 3.0% CO_2, 0.1% CS_2, and 0.1% H_2S (vpc). It was used as such in most experiments since purification (after Wiebe, *et al.*[10]) did not alter the experimental results obtained in liquid solution. Benzene, toluene, and *p*-xylene were Merck (Darmstadt) analytical grade. Benzene, treated with concentrated sulfuric acid, washed, dried with silica gel, and fractionally distilled, gave the same results as that of analytical grade. The olefins were Fluka pure grade. If they were contaminated with 1,3 dienes (vpc), the impurities were removed by refluxing the olefins over maleic anhydride followed by distillation.

A Rayonet Srinivasan–Griffin reactor, Model RPR-100 (Southern New England Ultraviolet Co.), equipped with 16 2537-Å mercury low-pressure Vycor lamps, was used for irradiation. Low-conversion irradiation experiments were performed at 28 ± 3° in 40-ml

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[1] For review articles, see H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, 4, 143 (1966); O. P. Strausz in "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience, New York, N. Y., 1967, Chapter 2; O. P. Strausz and H. E. Gunning in "The Chemistry of Sulfides," A. V. Tobolsky, Ed., Interscience, New York, N. Y., 1968, p 23.

[2] K. Gollnick and E. Leppin, *J. Amer. Chem. Soc.*, **92**, 2217 (1970).

[3] E. Leppin and K. Gollnick, *ibid.*, **92**, 2221 (1970).

[4] E. Leppin and K. Gollnick, *Mol. Photochem.*, **2**, 177 (1970).

[5] E. Leppin, K. Gollnick, and G. Schomburg, *Chromatographia*, **2**, 535 (1969).

[6] E. Leppin and K. Gollnick, *Chem. Ber.*, **103**, 2894 (1970).

[7] M. W. Schmidt and E. K. C. Lee, *J. Chem. Phys.*, **51**, 2024 (1969).

[8] W. H. Breckenridge and H. Taube, *ibid.*, **52**, 1713 (1970).

[9] E. Leppin and K. Gollnick, *Chem. Ber.*, **103**, 2571 (1970).

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

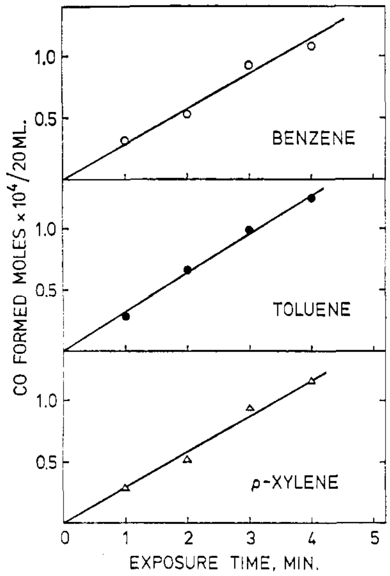

Figure 1. Formation of carbon monoxide as a function of exposure time during irradiation of saturated solutions of COS in benzene (○), toluene (●), and *p*-xylene (△).

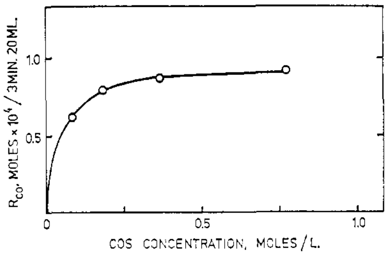

Figure 2. Rate of carbon monoxide formation as a function of COS concentration in benzene.

cylindrical quartz vessels which contained 20 ml of solution, whereas 200-ml cyclindrical quartz vessels equipped with a cold finger and containing 100–150 ml of solution were used for runs on a preparative scale. In order to prevent irradiation of the gas phase, the latter was protected with black polyethylene foil.

COS concentrations of saturated solutions were determined gas chromatographically by comparing COS peak areas generated by measured samples of the solutions with those obtained from known amounts of gaseous COS. The solubility coefficients thus determined were used to calculate concentrations of diluted solutions of COS, the dead-space volume in all low-conversion runs being equal to the volume occupied by the solution.

Prior to irradiation, oxygen was removed from the samples by conventional vacuum degassing at liquid nitrogen temperature on a mercury-free vacuum system.

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

The condensable fraction was analyzed by vapor-phase chromatography using a 2-m stainless steel column with 10% silicone oil DC-200 on 60/80 Chromosorb R and a 6-m stainless steel column with 5% silicone rubber SE 52 on 60/80 Chromosorb G, operated on a Perkin-Elmer (Bodenseewerk) fractometer F-6 and a Mikro Tek Model DSS-172 chromatograph, respectively, with flame ionization detector. Preparative vpc separations were performed on a 2-m glass column with 8% silicone gum rubber on 60/80 Chromoport XXX (Mikro Tek) using a Hewlett-Packard F and M Model 700 chromatograph with a thermal conductivity detector. If the amounts of reaction products were too small for direct gas chromatographic analysis of the irradiated solution, most of the starting material was removed by low-temperature distillation at reduced pressure before analyzing the reaction mixture.

Identification of reaction products was achieved by comparing retention times with those of authentic samples, by mass spectrometry, and in some cases by ir and nmr spectroscopy.

For quantitative determinations, the method of internal standard was employed after calibration of the detector of the vpc apparatus.

Quantum yields were determined by the uranyl oxalate actinometer (0.001 *M* UO_2SO_4 and 0.005 *M* $H_2C_2O_4$ solution) assuming a quantum efficiency of $\Phi_{2537} = 0.62$ for the oxalate decomposition. No filters were used, since 95% of the output of the light source between 3300 (absorption limit of the actinometer solution) and 2200 Å (transmission limit of Vycor) occurred at 2537 Å.

Results

(a) Photolysis of COS at 2537 Å in the Absence of Olefins. Irradiation of COS-saturated benzene solutions ($[COS]_s = 0.77$ *M* at 25° and 1 atm[2]) produced carbon monoxide and elemental sulfur. Even after longer periods of irradiation only traces of thiophenol could be observed by its characteristic smell and by gas chromatography. Similarly, irradiation of COS-saturated solutions of toluene ($[COS]_s = 0.73$ *M* at 25° and 1 atm[2]) and *p*-xylene ($[COS]_s = 0.685$ *M* at 25° and 1 atm[2]) yielded CO and elemental sulfur. Again, in either case a mercaptanous smell of the irradiated solutions was observed, but no mercaptans could be detected gas chromatographically, because they were formed in quantities lower than the limit of detection of our gas chromatographic analysis.

In all these cases CO formation is linearly dependent upon the irradiation time, at least for low-conversion runs (Figure 1). Deviations from linearity did occur, however, after prolonged irradiation, since then the solution became turbid as a result of the precipitation of elemental sulfur. The rates and quantum yields of CO formation determined from low-conversion runs are given in Table I.

Table I. Rate of Formation and Quantum Yield of CO from the COS Photolysis at 2537 Å in Aromatic Hydrocarbons

Solvent	$[COS]_s$, *M*	*R*, mol × 10^4 [c] CO	 Mercaptan	Φ(CO)
Benzene	0.77	0.84	0.004[a]	0.53
Toluene	0.73	0.95	*b*	0.59
p-Xylene	0.68	0.87	*b*	0.54

[a] Thiophenol. [b] Could not be determined. [c] Per 3 min, 20 ml.

Rates of CO formation as well as CO quantum yields are very similar in all three solvents and were found to be practically independent of the COS concentration between 0.25 and 0.7 *M* COS. At COS concentrations lower than 0.25 *M*, the rate of CO formation decreases. Figure 2 shows the results obtained with various COS concentrations in benzene.

(b) Photolysis of COS at 2537 Å in the Presence of Olefins. Cyclohexene. COS photolysis in benzene and toluene as well as in *p*-xylene in the presence of 0.6 *M* cyclohexene resulted in the formation of CO, elemental sulfur, and one single new compound, cyclohexene episulfide, which was isolated by preparative vpc and identified by comparison of its gas chromatographic retention time with that of an authentic sample[11] and by its ir[12] and mass spectra (see Table II). The mass spectrum, however, differed considerably from that published by Lown, *et al.*,[13] probably be-

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[11] "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., p 232.

[12] N. Sheppard, *Trans. Faraday Soc.*, **46**, 429 (1950).

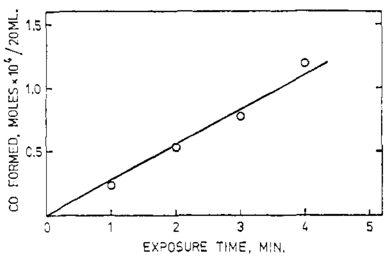

Figure 3. Formation of carbon monoxide as a function of exposure time in *p*-xylene in the presence of 0.6 *M* trimethylethylene; [COS] = 0.65 *M*.

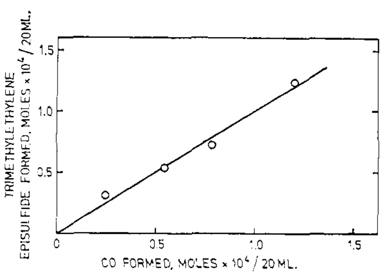

Figure 4. Formation of trimethylethylene episulfide *vs.* formation of carbon monoxide in *p*-xylene in the presence of 0.6 *M* trimethylethylene; [COS] = 0.65 *M*.

cause we used a mass spectrometer with a cooled-probe system. No other reaction products, in particular no cyclohexenethiol,[13] could be detected.

It is now well recognized that in the gas phase as well as in liquid solution excited aromatic hydrocarbons may react with olefins to give cycloaddition products[14] as well as transfer of electronic energy[15] to the olefins followed by either cis–trans isomerization[16] or dimerization.[17] Irradiation of a 0.6 *M* solution of cyclohexene in benzene or toluene at 2537 Å in the absence of COS produced a high-boiling material which contained some six different compounds with vpc retention times appropriate for C_{12} hydrocarbons. Since none of these compounds was formed in the presence of COS, the mixture, probably containing cyclohexene dimers[18] and adducts between the aromatic hydrocarbon and cyclohexene, was not further analyzed.

1-Hexene, 1-Heptene, 1-Octene, and Cyclopentene. Irradiation of 0.6 *M* solutions of these olefins in benzene saturated with COS yielded the corresponding episulfides as the sole products besides CO and elemental sulfur. Again, alkenethiols and benzene–olefin adducts or olefin dimers could not be detected. The episulfides were isolated by preparative vpc and identified by comparison of their gas chromatographic retention times with those of authentic samples.[19] Their ir spectra showed strong absorption bands at about 600 cm^{-1} which have been assigned to the C–S stretching vibration of ethylene sulfide.[19,20] The mass spectra are recorded in Table II. The mass spectrum of cyclopentene episulfide obtained in this work differs from that reported by others;[13] to our knowledge, mass spectra of the other episulfides of Table II have not yet been published.

Irradiation of COS-saturated benzene solutions in the presence of olefins may be used to produce episulfides on a preparative scale. With the above-mentioned photochemical reactor, about 120 to 180 mg (~10^{-3} mol) of episulfides may be obtained in 1 hr.

Cyclooctene, Cycloheptene, and Trimethylethylene. Of these olefins, cyclooctene seemed particularly interesting since it has been reported to add very easily to excited benzene[14c] and to be isomerized to the trans isomer by excited xylene.[16d] In the presence of COS, however, carbon monoxide, elemental sulfur, and cyclooctene episulfide (mp 25°)[21] were the only products. The ir spectrum of cyclooctene episulfide[21] shows strong bands at 630 and 1038 cm^{-1} and a band of medium intensity at 1140 cm^{-1}; its nmr spectrum is practically identical with that of the epoxide. For the mass spectrum, see Table II.

Similarly, cycloheptene episulfide was the only reaction product besides CO and elemental sulfur when COS and cycloheptene were irradiated in benzene. Again, the episulfide was identified by its ir, nmr, and mass spectra (Table II).

The episulfide of trimethylethylene was prepared by irradiation in *p*-xylene.[22] Its nmr spectrum (CCl_4, TMS as an internal standard) shows two doublets at δ 1.48 (3 H, J = 6 cps) and 1.55 (6 H, J = 0.8 cps) and one quartet at 2.75 ppm (1 H, J = 6 cps); its ir spectrum contains strong absorption bands at 590, 1038, and 1082 cm^{-1}; and its mass spectrum agrees fairly well with that reported by others.[13]

(c) Rates of Product Formation in the Presence of Olefins. A linear dependence of the formation of carbon monoxide on exposure time is observed when a 0.65 *M* COS solution in *p*-xylene is irradiated in the presence of 0.6 *M* trimethylethylene (Figure 3). Comparison of Figure 3 with Figure 1 shows that the rate of CO formation is independent of whether the olefin is present or not. The same linear dependence of CO formation upon exposure time and thus the same rates of CO formation were found for irradiations of COS in benzene in the presence of 0.6 *M* cyclohexene or 0.6 *M* 1-octene.

Similarly, the formations of the episulfides show linear time dependences, as is demonstrated for trimethylethylene episulfide production in Figure 4. Trimethylethylene episulfide formation is plotted *vs.* CO formation for various exposure times when 0.65 *M*

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[13] E. M. Lown, E. L. Dedio, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **89**, 1056 (1967).

[14] (a) R. Srinivasan and K. A. Hill, *ibid.*, **87**, 4653 (1965); (b) K. E. Wilzbach and L. Kaplan, *ibid.*, **88**, 2066 (1966); (c) D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Commun.*, 512 (1966); (d) A. Morikawa, S. Brownstein, and R. J. Cvetanović, *J. Amer. Chem. Soc.*, **92**, 1471 (1970); for a review see (e) D. Bryce-Smith, *Pure Appl. Chem.*, **16**, 47 (1968).

[15] R. B. Cundall and P. A. Griffiths, *Chem. Commun.*, 194 (1966).

[16] (a) R. B. Cundall and P. A. Griffiths, *Trans. Faraday Soc.*, **61**, 1968 (1965); (b) M. A. Golub, C. L. Stephens, and J. L. Brash, *J. Chem. Phys.*, **45**, 1503 (1966); (c) E. K. C. Lee, H. O. Denschlag, and G. A. Haninger, Jr., *ibid.*, **48**, 4547 (1968); (d) J. S. Swenton, *J. Org. Chem.*, **34**, 3217 (1969); see also (e) J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969).

[17] (a) P. J. Kropp, *J. Amer. Chem. Soc.*, **89**, 3650 (1967); (b) P. J. Kropp and H. J. Krauss, *ibid.*, **89**, 5199 (1967).

[18] That cyclohexene dimerizes upon electronic energy transfer from a suited donor may be inferred from a private communication of D. R. Arnold to P. J. Wagner and G. S. Hammond, quoted by these authors in *Advan. Photochem.*, **5**, 21 (1968).

[19] For leading references on the preparation of thiiranes, see M. Sander, *Chem. Rev.*, **66**, 297 (1966).

[20] G. B. Guthrie, Jr., D. W. Scott, and G. Waddington, *J. Amer. Chem. Soc.*, **74**, 2795 (1952).

[21] D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **28**, 2932 (1963); **29**, 2702 (1964).

[22] Benzene is less suited as solvent since small quantities of trimethylethylene episulfide are hardly separable from excess benzene because of their similar boiling points.

Table II. Mass Spectra of Episulfides[a]

	Episulfide												
	1-Hexene		1-Heptene		1-Octene		c-Pentene		c-Hexene		c-Heptene	c-Octene	
	Relative intensity at ionization voltage, V												
m/e	70	18	70	18	70	13	70	15	70	12	70	70	18
39	42		37		30		*100*		27		36	24	
40							41				13	14	
41	*100*		*100*		*100*		62		28		35	36	
42	67	34	42		21		17						
43	51	20	16		35								
45			13		30		18		18		18		
47					20								
53					11		54		21		19	11	
54			17	16	23		14		30		45	39	14
55	67	22	91	25	85						32	17	
56	91	75	86	*100*	23								
57			24	21									
59					14								
60					21				22				
65							35						
66							52	27			23		
67	12	17	14	14	27		90	79	34		66	*100*	47
68		11		14	20		92	34			32	20	17
69	28	35	30	29	57	10							
70			42	60	15								
71							17		11				
73					12				18		13		
74	20	25	32	40	58								
77									10		11		
78							13						14
79									42		36	11	
80									66	22	10		18
81			19	34	30				*100*	19	34	25	32
82		18			12	19	27		18	26		34	70
83				20		13		18					11
84	43	*100*											
85							26	23	12				
87			12	14	22								
89				13									
91												16	
95											*100*		18
96				42							30		
97				17									
98			26	80									
99							11	13					
100							73	*100*					
101				27									
106												12	57
109												23	58
110					15	99						22	*100*
111						29							12
114									64	*100*			
115					12	67							
116	21	66											
128											52		
130			27	98									
142												21	98
143													14
144					15	*100*							

[a] The spectra were obtained on an Atlas CH-5 mass spectrometer with cooled-probe system.

COS in *p*-xylene is irradiated in the presence of 0.6 *M* trimethylethylene. In this case, the amount of episulfide formed is equal to that of CO. However, if the other olefins were applied at concentrations of 0.6 *M*, the yields of episulfides were always lower than those of carbon monoxide.

It has been shown that in the absence of olefins the CO rate does not depend upon the COS concentration between 0.3 and 0.7 *M* COS, and the same is true if 1 *M* or less of cyclohexene or 1-octene is present (Figure 5). However, if, *e.g.*, the concentration of added cyclohexene or trimethylethylene exceeds 1.5 *M*, the CO rate decreases appreciably. At such high olefin concentrations, the olefins may compete with COS for the excited aromatic hydrocarbons, thus decreasing the rates of CO formation. In general, however, the experimental conditions were chosen such that the olefins did not interfere with the COS decomposition. This was found to be always the case if the concentration ratio [COS]/[olefin] was equal to or greater than 0.5.

Finally, the rate of episulfide formation as a function of the olefin concentration was studied with trimethylethylene (Figure 6) and cyclohexene (Figure 7). Within the concentration range studied from about 0.05 to 1 *M* olefin, the rate of trimethylethylene episulfide formation is independent of the concentration of tri-

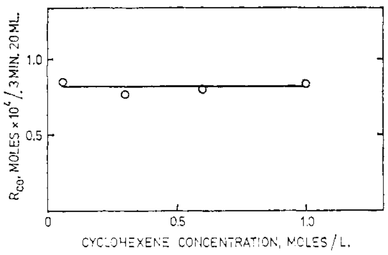

Figure 5. Rate of CO formation in benzene as a function of the concentration of added cyclohexene; [COS] = 0.65 *M*.

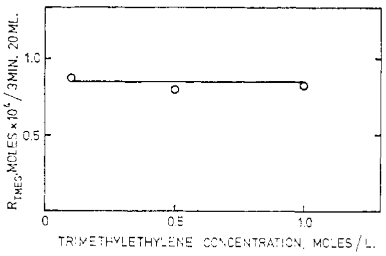

Figure 6. Rate of formation of trimethylethylene episulfide (TMES) as a function of trimethylethylene concentration in *p*-xylene; [COS] = 0.65 *M*.

methylethylene and equal to the rate of CO formation, whereas with cyclohexene, the rate of episulfide formation depends very much upon the cyclohexene concentration. Even at the highest concentration studied the rate of episulfide production does not exceed about one-half of that of CO formation.

Thus, the two olefins exhibit different reactivities toward episulfide formation although neither of them did interfere with the COS decomposition at the concentrations studied.

Discussion

As may be inferred from the extinction coefficients listed in Table III, COS in benzene, toluene, and *p*-xylene absorbs only a very small fraction of the incident light. The molar concentrations of the aromatic hydrocarbons are about 10 times that of COS and the molar extinction coefficients of those hydrocarbons at 2537 Å are even about a 100 times that of COS. It is obvious then that the photolysis of COS in these solvents is sensitized by the aromatic hydrocarbons.

Table III. Extinction Coefficients and Electronic Excitation Energies of COS, Benzene, Toluene, and *p*-Xylene

	ϵ_{2537}, M^{-1} cm^{-1}	E_S,[a] kcal/mol	E_T,[b] kcal/mol
COS	2.5	106,[c,e] 100[d,e]	80[e]
Benzene	250[f]	108[g]	84[g]
Toluene	180[f]	106[g]	83[g]
p-Xylene	190[f]	105[g]	80.4[g]

[a] Energy of the lowest excited singlet state. [b] Triplet energy. [c] Lowest stable excited singlet. [d] Energy requirement for process 1. [e] From ref 4. [f] From "UV-Atlas of Organic Compounds," Vol. I-IV, Butterworths, London, and Verlag Chemie, Weinheim/Bergstr., Germany, 1966-1968. [g] From Landolt-Börnstein, "Luminescence of Organic Substances," Vol. II, Part 3, New Series, Springer-Verlag, Berlin, 1967.

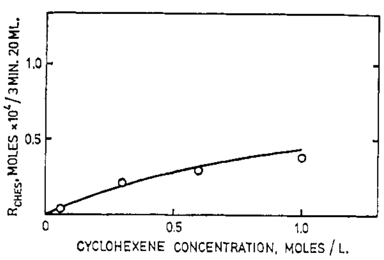

Figure 7. Rate of formation of cyclohexene episulfide (CHES) as a function of cyclohexene concentration in benzene; [COS] = 0.65 *M*.

From an energetical point of view, singlet–singlet as well as triplet–triplet energy transfer from the aromatic hydrocarbons to COS may occur (Table III). As will be discussed in a subsequent paper,[23] both processes seem to be involved in the COS decomposition.

The CO quantum yield is independent of whether olefins are present or not during the sensitized COS photolysis. However, elemental sulfur is formed almost exclusively in the absence of olefins, whereas part or even all of the sulfur formed can be trapped as an episulfide in the presence of olefins. This renders an excited molecule mechanism for the product forming step as depicted in eq 2 very unlikely. In fact, we conclude that the photolysis of COS sensitized by benzene, toluene, and *p*-xylene leads to sulfur *atoms* and carbon monoxide in the primary process as is the case in the direct photolysis of COS.

$$\mathrm{COS} \xrightarrow[\text{sensitizer}]{h\nu} \mathrm{COS}^* \xrightarrow{+\text{olefin}} \text{episulfide} + \mathrm{CO} \qquad (2)$$

From the fact that in the presence of olefins only episulfides but no mercaptans are formed, we may conclude that the sulfur atoms which react with the olefinic double bonds are in the triplet P state. If they were in the singlet D state, appreciable amounts of mercaptans would be expected, as has been observed in the gas phase.[1] Thus, ^{1}D sulfur atoms are either not formed in the sensitized reaction or are very rapidly converted to ^{3}P sulfur atoms by some "solvent-catalyzed" process.[2,3,23] From the occurrence of traces of thiophenol one may suspect that S(^{1}D) atoms are present during the COS photolysis in benzene at least in small concentrations.

It has been demonstrated[2,3] that during direct photolysis in solution at [COS] $\leqslant$ 0.7 *M* neither S(^{1}D) atoms nor S(^{3}P) atoms react with COS according to

$$\mathrm{S(^1D)} + \mathrm{COS} \longrightarrow \mathrm{S_2} + \mathrm{CO} \qquad (3a)$$

$$\mathrm{S(^3P)} + \mathrm{COS} \longrightarrow \mathrm{S_2} + \mathrm{CO} \qquad (3b)$$

Obviously, this holds also for the sensitized reaction. Otherwise, the CO rate and CO quantum yield should depend on the concentration of COS as well as on the concentration and nature of the added olefins. This, however, is not the case except for very high olefin concentrations where reactions between the excited aromatic hydrocarbon and the olefins become appreciable and consequently decrease the sensitized COS decomposition. Therefore, as has been found for the direct COS photolysis in liquid solution,[2,3] all S(^{3}P) atoms which do not form products will recombine

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(23) E. Leppin and K. Gollnick, to be submitted for publication.

to give S_2 molecules which in turn give rise to the formation of elemental sulfur.

We observed, however, a dependence of the CO quantum yield on the COS concentration in benzene at COS concentrations below about 0.2 *M* COS. We suspect that at such small concentrations energy transfer from excited benzene becomes rather inefficient, since excited singlet as well as triplet benzene molecules are known to possess rather short lifetimes in liquid benzene.[24,25] The following simple mechanism

$$\mathrm{COS} \xrightarrow[\text{aromatic sensitizer}]{h\nu} \longrightarrow \mathrm{CO} + \mathrm{S}(^3\mathrm{P}) \tag{4}$$

$$\mathrm{S}(^3\mathrm{P}) + \text{olefin} \longrightarrow \text{episulfide} \tag{5}$$

$$2\mathrm{S}(^3\mathrm{P}) + \mathrm{M}(\text{solvent}) \longrightarrow \mathrm{S}_2 \longrightarrow \mathrm{S}_8 \tag{6}$$

accounts for all the experimental facts observed. The detailed mechanism of reaction 4 will be presented in a subsequent paper.[23]

Assuming steady-state conditions for $[\mathrm{S}(^3\mathrm{P})]$, the following kinetic expressions may be derived, where R_{ES} = rate of episulfide formation.

$$R_{\mathrm{ES}} = k_5[\text{olefin}][\mathrm{S}(^3\mathrm{P})] \tag{7}$$

$$R_{\mathrm{CO}} = k_5[\text{olefin}][\mathrm{S}(^3\mathrm{P})] + k_6[\mathrm{S}(^3\mathrm{P})]^2 \tag{8}$$

Let us consider the two limiting cases of reactivity. (a) If the olefin is very reactive toward sulfur atoms, the rate of reaction 6 may become negligible as compared with that of reaction 5, leading to

$$R_{\mathrm{ES}} = R_{\mathrm{CO}} \tag{9}$$

i.e., the rate of episulfide formation will be equal to the CO rate and independent of the olefin concentration. This is exemplified in the case of trimethylethylene (*cf.* Figure 6). (b) If the rate of reaction of $\mathrm{S}(^3\mathrm{P})$ atoms with an added olefin is slow as compared with the rate of recombination of the sulfur atoms, the mechanism predicts a linear dependence of the rate of episulfide formation upon the olefin concentration.

$$k_5[\text{olefin}][\mathrm{S}(^3\mathrm{P})] \ll k_6[\mathrm{S}(^3\mathrm{P})]^2 \tag{10}$$

$$R_{\mathrm{ES}} = k_5\sqrt{R_{\mathrm{CO}}/k_6}[\text{olefin}] \tag{11}$$

Cyclohexene may be envisaged as an example for the latter case (*cf.* Figure 7). The slight curvature indicates that condition 10 is only fulfilled at low cyclohexene concentrations. The slope at the origin of the curve of Figure 7 may be used to get a rough estimate of the rate constant of cyclohexene episulfide formation, k_5(cyclohexene). With $R_{\mathrm{CO}} = 0.85 \times 10^{-4}$ mol/(3 min 20 ml) (Figure 5), reaction 6 assumed to be diffusion controlled ($k_6 \approx 10^{10}$ M^{-1} sec^{-1}), and a slope of 0.7×10^{-4} l./(3 min 20 ml) = 2×10^{-5} sec^{-1}, the rate constant of cyclohexene episulfide formation from $\mathrm{S}(^3\mathrm{P})$ atoms and cyclohexene in liquid solution is calculated to be k_5(cyclohexene) = 4×10^2 M^{-1} sec^{-1}. Using eq 7 and 8 for calculation and assuming a diffusion-controlled rate for reaction 6, the corresponding rate constant k_5(trimethylethylene) is then estimated to be equal to or greater than 10^4 M^{-1} sec^{-1} in order to explain the trapping of at least 90% of the $\mathrm{S}(^3\mathrm{P})$ atoms by this olefin at an olefin concentration of 0.1 *M*.

Both rate constants are surprisingly low as compared to $k_5 = 10^7$–10^8 M^{-1} sec^{-1} derived for the gas-phase reactions of $\mathrm{O}(^3\mathrm{P})$, $\mathrm{S}(^3\mathrm{P})$, $\mathrm{Se}(^3\mathrm{P})$, and $\mathrm{Te}(^3\mathrm{P})$ atoms with ethylene.[26,27] The reduced reactivity of $\mathrm{S}(^3\mathrm{P})$ in episulfide formation in liquid benzene might indicate the participation of solvent-complexed triplet sulfur atoms during the product-forming step.

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