The Benzene-photosensitized Decomposition of Carbonyl Sulfide in a Cyclohexane Solution

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The decomposition of carbonyl sulfide photosensitized by benzene in the solution of cyclohexane has been investigated at room temperature. The quantum yield of CO formation, ϕ_{CO}, at an infinite concentration of COS was estimated to be 1.0. The COS concentration dependence of ϕ_{CO} corresponded well to that of the quenching efficiency of COS on benzene fluorescence. These results suggest that, of the two possible photosensitization processes:

$$C_6H_6(^1B_{2u}) + COS \longrightarrow C_6H_6 + CO + S(^1D)$$

and

$$C_6H_6(^3B_{1u}) + COS \longrightarrow C_6H_6 + CO + S(^3P),$$

the former is responsible for the formation of CO. The very small yield of cyclohexanethiol may be explained by the fact that benzene is an efficient catalyzer for the transition process, $S(^1D) \rightarrow S(^3P)$.

When electronically excited at around 5 eV, carbonyl sulfide has two energetically-possible decomposition channels. The one is through an excited singlet state:

$$COS = CO(^1\Sigma^+) + S(^1D) \qquad \Delta H = 98.8 \text{ kcal/mol}$$

the other is through a triplet:

$$COS = CO(^1\Sigma^+) + S(^3P) \qquad \Delta H = 72.4 \text{ kcal/mol}$$

Therefore, the benzene-photosensitized decomposition of carbonyl sulfide at 2537 Å, if it occurs, has two possible processes. The reaction mechanism may be described as follows:

$$C_6H_6 + h\nu \longrightarrow C_6H_6^*(^1B_{2u}) \qquad (1)$$

$$C_6H_6^* \longrightarrow C_6H_6 + h\nu_f \qquad (2)$$

$$C_6H_6^* \longrightarrow C_6H_6^{**}(^3B_{1u}) \qquad (3)$$

$$C_6H_6^{**} \longrightarrow C_6H_6 \qquad (4)$$

$$C_6H_6^* + COS \longrightarrow C_6H_6 + CO + S(^1D) \qquad (5)$$

$$C_6H_6^{**} + COS \longrightarrow C_6H_6 + CO + S(^3P) \qquad (6)$$

This report will be mainly concerned with which process, Reaction (5) or (6), is more important for the decomposition of carbonyl sulfide.

The gas-phase photolysis of carbonyl sulfide was extensively investigated by Gunning and Strausz.[1] Regarding the liquid-phase, Gollnick and Leppin reported several important observations.[2] When COS is photolyzed at 2537 Å in liquid alkanes such as cyclohexane and cyclopentane, the quantum yield of CO formation is 0.9 and that of mercaptan is in the range of 0.3—0.5. They also showed that methyl, ethyl, and isopropyl alcohols and acetonitrile efficiently catalyze the transition process, $S(^1D) \rightarrow S(^3P)$.

Recently, we showed that COS molecules act as effective electron scavengers in the radiolysis of benzene.[3] Consequently, the benzene-photosensitized decomposition of COS has become an urgent problem to be solved.

Experimental

The COS was a product of the Merck Company. Further purification was not made except for bulb-to-blub distillation, with the rejection of the head and tail fractions. The cyclohexane (Tokyo Kagaku Seiki Co., spectro grade) was passed through a 1 m silica-gel column before use. The benzene (Tokyo Pure Chemical Co., spectro grade) and ethylene (Takachiho Chemical Co.) were used as supplied.

A low-pressure mercury resonance lamp containing 5 Torr Ne was used for irradiating solutions at room temperature in a 30 m*l*, 1 cm thick, cylindrical quartz vessel. The solution was stirred with a magnetic stirrer in order to maintain the homogeneity of the solute concentration. The irradiating light was passed through a Toshiba UV-25 glass filter to cut off the wavelengths shorter than 2000 Å. The reaction vessel was irradiated horizontally to let the gas produced escape from the reaction zone.

In order to estimate the light intensity, the mercury-photosensitized decomposition of ethylene was carried out in a reaction vessel of exactly the same size. The quantum yield of hydrogen at 45 Torr of ethylene was assumed to be 0.203.[4]

The benzene fluorescence spectra were measured using a Hitachi PMF-2A fluorometer. The exciting light was set at 2537 Å. The cell used for the measurement was modified so as to evacuate it and to introduce a quencher gas.

The gas noncondensable at the temperature of liquid nitrogen was collected and measured by means of a Toepler pump. After passing the gas through a cuprous oxide furnace at 390°C, the noncondensables at the temperature of dry ice-methanol were again collected and measured. Cyclohexanethiol and benzenethiol were analyzed, using a Hitachi 023 gas chromatograph equipped with a FID detector and a 1 m tricresylphosphate column at 80°C. Bromobenzene was used as a reference to estimate the absolute yield because its elution time is close to that of cyclohexanethiol.

The solubility of carbonyl sulfide in cyclohexane and in benzene was measured by a technique already reported.[5] Ostwald's coefficients obtained at 20°C are 8.0 in cyclohexane and 13 in benzene.

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[1] H. E. Gunning and O. P. Strausz, "Advances in Photochemistry," Vol. 4 ed. by W. A. Noyes, Jr., G.S. Hammond, and J. N. Pitts, Jr., Interscience Publishers, New York (1966), p. 143.

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

[3] S. Hirokami, S. Shishido, and S. Sato, This Bulletin, **43**, 973 (1970).

[4] B. DeB. Darwent, *J. Chem. Phys.*, **19**, 258 (1951).

[5] T. Saito, K. Takahashi, and S. Sato, This Bulletin, **41**, 2603 (1968).

Results

Benzene-photosensitized Decomposition of COS. A rather high concentration of benzene (0.43 mol/*l*) was used to prevent the direct photolysis of COS ($\varepsilon_{2537} \approx$ 10 *l* mol^{-1}cm^{-1}).[6] At this concentration, more than 99% of the impinging light at 2537 Å is absorbed in the solution. The quantum yield of CO is listed in Table 1 as a function of the COS concentration. The values of ϕ_{CO} may be a little overestimated, because the resonance line absorbed by mercury at room temperature is sharper than that emitted by the light source and because benzene molecules can absorb the foot of the resonance line. No gas noncondensable at 77°K other than CO could be obtained.

Table 1. The quantum yield of carbon monoxide in the benzene-photosensitized decomposition of carbonyl sulfide in the solution of cyclohexane

Benzene consentration is 0.43 mol/*l*

Concentration of COS 10^{-2} mol/*l*	Quantum yield of CO ϕ_{CO}
0.22	0.17
0.24	0.19
0.26	0.21
0.37	0.25
0.41	0.27
0.42	0.30
0.44	0.35
0.53	0.42
0.65	0.40
0.75	0.40
0.87	0.47
1.09	0.48
1.21	0.64
2.17	0.73
2.84	0.82
3.09	0.76

Gas-chromatographic analysis showed that cyclohexanethiol is the only product in the liquid. The formation of benzenethiol could not be detected. As the yield of cyclohexanethiol was very small, the benzene concentration dependence was checked. The results are shown in Fig. 1. Obviously, the presence of benzene severely prevents the formation of cyclohexanethiol. In the absence of benzene, the light is absorbed by COS and the [cyclohexanethiol]/[CO] ratio obtained is in agreement with that reported by Gollnick and Leppin.[2]

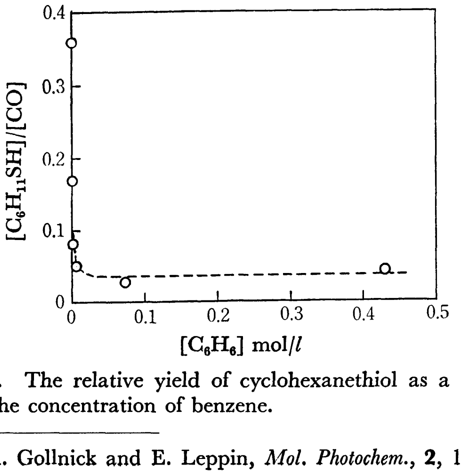

Fig. 1. The relative yield of cyclohexanethiol as a function of the concentration of benzene.

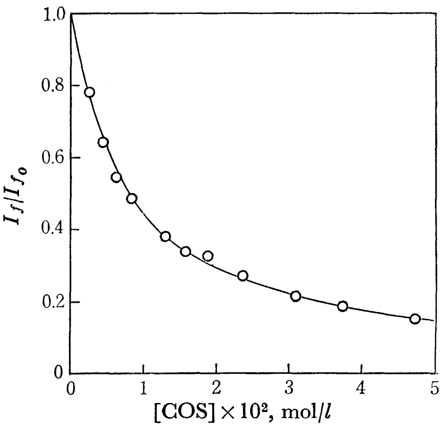

Fig. 2. The relative intensity of the benzene fluorescence as a function of the concentration of carbonyl sulfide.

Quenching of Benzene Fluorescence by COS. The benzene fluorescence was measured at 2800 Å, where the spectrum showed its maximum. In Fig. 2, the relative intensity of the fluorescence is plotted as a function of the concentration of COS. Exactly the same quenching curve was obtained by using the fluorescence intensity at a different wavelength (2950 Å). The benzene concentration used was 0.43 mol/*l*; the value was the same as that used for the photosensitized decomposition.

Discussion

The steady-state-treatment of the reaction mechanism described in the Introduction gives the following Stern-Volmer equation:

$$I_{f_0}/I_f = 1 + k_5\tau[\text{COS}] \qquad \text{(I)}$$

Here, I_{f_0} and I_f denote the fluorescence intensity in

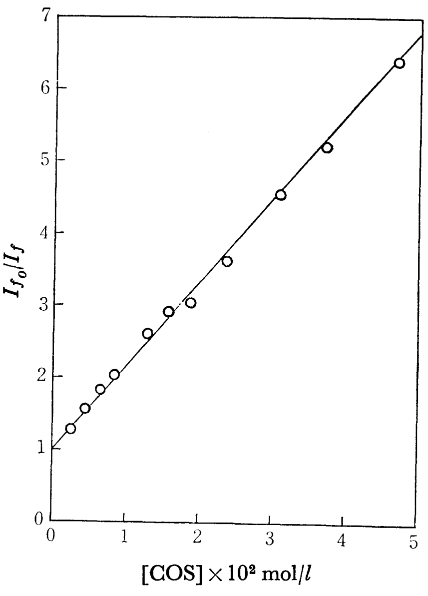

Fig. 3. The Stern-Volmer plot on the benzene fluorescence. The quencher is carbonyl sulfide.

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[6] K. Gollnick and E. Leppin, *Mol. Photochem.*, **2**, 179 (1970).

the absence and in the presence of the quencher, COS, respectively. k_5 is the rate constant of Reaction (5), and τ is the lifetime of the $^1B_{2u}$ benzene in this solution. From the linear relationship shown in Fig. 3, the $k_5\tau$ value could be calculated to be 110 ± 10 *l*/mol by the least-squares method. This value may be compared with 300 *l*/mol, the value which was obtained in the gas phase.[7]

Since the CO formation has two possible channels, the quantum yield of CO has a somewhat complicated dependence on the concentration of COS.

$$\phi_{\mathrm{CO}}^{-1} = \left(1+\frac{1}{k_5\tau[\mathrm{COS}]}\right)\left(1+\frac{k_3k_6}{k_5k_6[\mathrm{COS}]+k_5/\tau'}\right)^{-1} \qquad \text{(II)}$$

Here, τ' is the lifetime of the $^3B_{1u}$ benzene in the solution. If only one of the two possible channels is operative for the formation of CO, Eq. (II) can be simplified as follows:

$$\phi_{\mathrm{CO}}^{-1} = A^{-1}\left(1+\frac{1}{B[\mathrm{COS}]}\right) \qquad \text{(III)}$$

In the case of the channel through the singlet-excited state, $A \leq 1$ and $B = k_5\tau$, while in the case of the channel through the triplet state, A cannot exceed the quantum yield of the intersystem crossing, ϕ_{SC} and $B = k_6\tau'$. Figure 4 shows the reciprocal of the yield of CO as a function of the reciprocal of the COS concentration. Although the plots are a little scattered, the least-squares method gives $A \approx 1.0$ and $B = 80 \pm 30$ *l*/mol. This value of B roughly agrees with the $k_5\tau$ value obtained by the measurement of the fluorescence quenching.

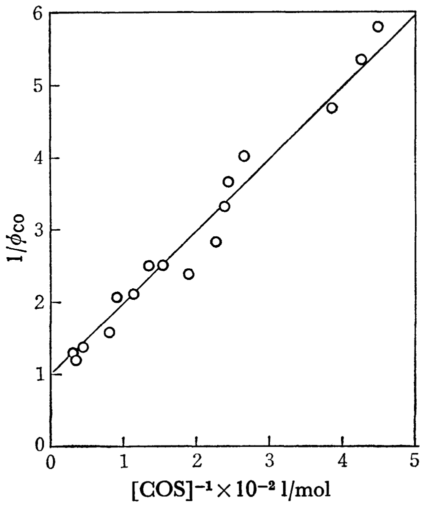

Fig. 4. The reciprocal of the quantum yield of carbon monoxide as a function of the reciprocal of the concentration of carbonyl sulfide.

The lifetime of the $^1B_{2u}$ benzene in cyclohexane at room temperature is reported to be 29 nsec, where the concentration of benzene is 3.4×10^{-2} mol/*l*.[8] Ludwig and Amata observed that the lifetime in *n*-nonane is a little dependent upon the concentration of benzene, but its value is not smaller than 26 nsec, even in pure benzene.[9] In the present discussion, therefore, τ may be assumed to be 29 nsec.

The situation is very obscure for the lifetime of the $^3B_{1u}$ benzene. Cundall *et al.* estimated that the lifetime in pure benzene is of the order of 10 nsec.[10] In a previous paper, we investigated the benzene-photosensitized isomerization of butene-2 in a solution of cyclohexane and estimated the lifetime of the $^3B_{1u}$ benzene to be of the order of 0.1 μsec at 5×10^{-4} mol/*l* of benzene.[11]

Consequently, the agreement between the B value and the $k_5\tau$ value obtained in the fluorescence measurement cannot establish that Reaction (5), the singlet-singlet energy transfer, is responsible for the formation of CO. If the triplet-triplet energy transfer, Reaction (6), is responsible for this process, however, the A value should be equal to or less than ϕ_{SC}. Our previous paper showed that ϕ_{SC} is less than 0.25, while Cundall *et al.* estimated that ϕ_{SC} in pure benzene is 0.6. The present experiment obviously shows that the quantum yield of CO at an infinite concentration of COS is much higher than 0.6. As stated in the Results section, the quantum yields obtained in the present experiment may be a little overestimated. The error is probably within 10%, however, because the quantum yield of cyclohexanethiol in the absence of benzene is in good agreement with that reported by Gollnick and Leppin.[2]

Thus, the discussion of the B factor could not distinguish whether Reaction (5) or Reaction (6) is responsible for the formation of CO, but that of the A factor strongly suggested that Reaction (5) is responsible. It may be concluded, therefore, that the CO formation in the benzene-photosensitized decomposition of COS in cyclohexane results from the singlet-singlet energy transfer. As has been stated above, the $k_5\tau$ value is 80—110 *l*/mol. The k_5 value, therefore, is $3.3 \pm 0.6 \times 10^9$ *l*/mol sec. This value suggests that Reaction (5) is diffusion-controlled.

As was shown in the Results section, the presence of benzene severely hindered the formation of cyclohexanethiol. This is probably because benzene molecules effectively catalyze the transition process, $\mathrm{S}(^1D) \rightarrow \mathrm{S}(^3P)$. In the benzene-photosensitization, the following process may be operative:

$$\begin{aligned} \mathrm{C_6H_6}(^1B_{2u}) + \mathrm{COS} &\longrightarrow \mathrm{C_6H_6}\cdots\mathrm{S} + \mathrm{CO} \\ &\longrightarrow \mathrm{C_6H_6} + \mathrm{S}(^3P) + \mathrm{CO} \end{aligned}$$

Here, $\mathrm{C_6H_6}\cdots\mathrm{S}$ represents the intermediate complex.

Since the benzene concentration used in the present experiment is high, the formation of the benzene singlet excimer cannot be ruled out. If the excimer formation is included in the reaction mechanism, the steady-state-treatment becomes a little more complicated. However, the conclusion of the singlet-singlet energy transfer cannot be altered regardless of whether or not the

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[7] E. K. Lee, M. W. Schmidt, R. G. Shortridge, Jr., and G. A. Haninger, Jr., *J. Phys. Chem.*, **73**, 1805 (1969).

[8] I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York and London (1965), p. 42.

[9] P. K. Ludwig and C. D. Amata, *J. Phys. Chem.*, **72**, 3725 (1968).

[10] R. B. Cundall, G. B. Evans, P. A. Griffiths, and J. P. Keene, *ibid.*, **72**, 3871 (1968).

[11] S. Sato, H. Kobayashi, and K. Fukano, *Kogyo Kagaku Zasshi*, **72**, 209 (1969).

excimer is quenched by COS.

In this work, the presence of the $^3E_{1u}$ state (4.5 eV) of benzene is completely ignored because its property is unknown. If the property becomes apparent, the inclusion of this state in the reaction mechanism can be easily done.