THE MERCURY-PHOTOSENSITIZED REACTION OF TETRAHYDRO-THIOPHENE-1, 1-DIOXIDE (SULFOLANE)
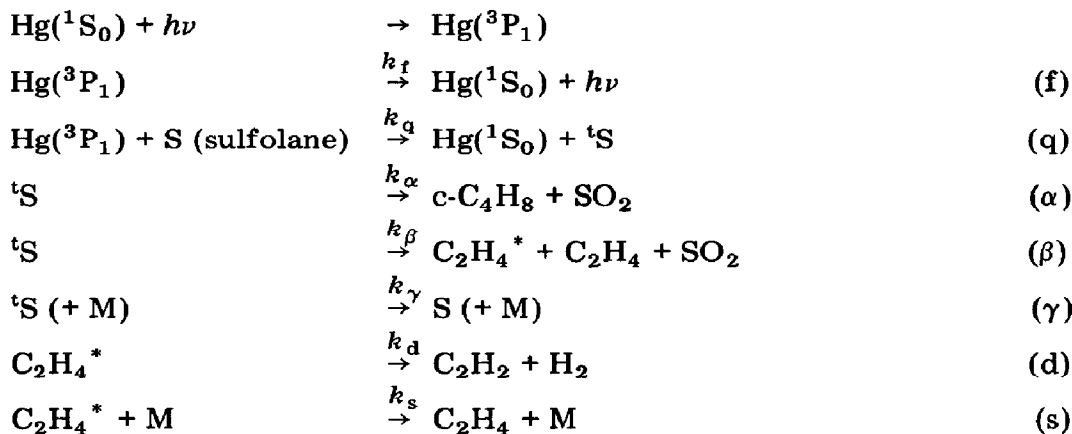
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Summary

The mercury-photosensitized reaction of tetrahydrothiophene-1,1-dioxide (hereafter called sulfolane) was studied in the vapor phase in the temperature range 70 - 130 °C. The major products are SO_2, C_2H_4, C_2H_2 and c-C_4H_8, and the minor products are CH_4, C_2H_6, C_3H_8 and C_3H_6. From a study of pressure effect of sulfolane and several quenching gases on the rate ratios $R_{C_2H_4}/R_{C_2H_2}$ and $R_{c\text{-}C_4H_8}/R_{C_2H_2}$, the formation of energy-rich ethylene and normal ethylene in equal amounts is presumed, and the following reaction scheme is proposed:

$$Hg(^1S_0) + h\nu \quad \rightarrow \quad Hg(^3P_1)$$

$$Hg(^3P_1) \quad \overset{h_f}{\rightarrow} \quad Hg(^1S_0) + h\nu \tag{f}$$

$$Hg(^3P_1) + S \text{ (sulfolane)} \quad \overset{k_q}{\rightarrow} \quad Hg(^1S_0) + {}^tS \tag{q}$$

$${}^tS \quad \overset{k_\alpha}{\rightarrow} \quad c\text{-}C_4H_8 + SO_2 \tag{α}$$

$${}^tS \quad \overset{k_\beta}{\rightarrow} \quad C_2H_4{}^* + C_2H_4 + SO_2 \tag{β}$$

$${}^tS \text{ (+ M)} \quad \overset{k_\gamma}{\rightarrow} \quad S \text{ (+ M)} \tag{γ}$$

$$C_2H_4{}^* \quad \overset{k_d}{\rightarrow} \quad C_2H_2 + H_2 \tag{d}$$

$$C_2H_4{}^* + M \quad \overset{k_s}{\rightarrow} \quad C_2H_4 + M \tag{s}$$
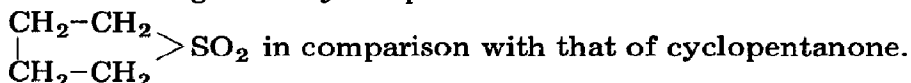
(${}^tS$ = triplet sulfolane; $C_2H_4{}^*$ = energy-rich ethylene)

The limiting values of quantum yields at high sulfolane pressure, Φ_{SO_2}, $\Phi_{c\text{-}C_4H_8}$ and $\Phi_{C_2H_4{}^*}$ were found to be 0.21, 0.04 and 0.17 respectively. From the pressure effect of the quenchers, the values k_s/k_d and k_α/k_β for sulfolane, SF_6, Xe, Ar, He and N_2 were determined.

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To elucidate further the detailed mechanism, mercury-photosensitized reaction of sulfolane-2,2,5,5-d_4 was carried out. From the analysis of the deuterated ethylenes, it is found that ethylene-d_2 is the major product. It is concluded that ethylene is formed through the fission of the C_3–C_4 bond of sulfolane.

Introduction

While the photochemistry of cyclic ketones [1], particularly cyclopentanone [2], has been studied in detail, little is known about the photochemical behavior of cyclic compounds containing a hetero atom as a ring member. Odaira et al. [3] reported that the irradiation of 1,3-dihydroisothianaphthene-2,2-dioxide with a low pressure mercury lamp accelerates its pyrolytic desulfonylation to give benzocyclobutene and dibenzocyclooctadiene. Cava et al. [4] presumed that the desulfonylation proceeds through a vibrationally highly excited singlet ground state, on the basis of the consideration that the photolytic products are similar to those of pyrolysis. On the other hand, Saltiel and Metts [5] found that the benzene-photosensitized reaction of 3-sulfolene gives butadiene derivatives, and they presumed that the intermediate of the photosensitized reaction of 3-sulfolene is a triplet, resulting in ring-opened products through conrotatory desulfonylation. Since no study has been reported on the photochemistry of saturated cyclic sulfones, it will be interesting to study the photochemical behavior of sulfolane
$$\begin{matrix} CH_2-CH_2 \\ | \qquad\quad \\ CH_2-CH_2 \end{matrix} > SO_2$$ in comparison with that of cyclopentanone.

Since sulfolane has only a very weak light absorption above 200 nm [6], the mercury-photosensitized reaction was investigated with the 253.7 nm mercury resonance line.

Experimental

Materials

Commercial sulfolane was dried with anhydrous $CaCl_2$ and distilled under reduced pressure. Sulfolane-2,2,5,5-d_4 was synthesized from sulfolene by successive deuterium exchange and hydrogenation [7], and its isotopic composition was determined by mass spectrometry to be: d_6, 1%; d_5, 10%; d_4, 84%; d_3, 5%; corrected for ^{13}C, ^{33}S, ^{34}S, ^{17}O and ^{18}O, and it was confirmed also by proton n.m.r. that it has only a negligible fraction of d_3–d_0 compounds. SO_2, NO, SF_6, C_2H_4, Xe, N_2O and C_2H_6 were used after trap-to-trap distillation. N_2, He and Ar were used without further purification.

Apparatus

For light irradiation, reaction vessels of two different types, type I and

type II, were used. The type I vessel consisted of a cylindrical cell of quartz (5 cm in diameter, and 2 cm in length), a Pyrex bulb of 500 ml with a finger, a Pyrex circulating fan, and a breakable seal, and this type of vessel was used for the usual experiments. The type II vessel had a much smaller volume in order to transfer the products into a gas–liquid chromatography (g.l.c.) cell as much as possible, and was used for the experiments in the presence of large amounts of quenching gas. It consisted of a cylindrical quartz cell (5 cm in diameter and 1 cm in length), and a Pyrex bulb, with a total volume of 40 ml. The low-pressure mercury lamp was laboratory fabricated, and it was operated keeping the electrode parts at 50 °C by circulating water. To cut out 184.9 nm light, a Vycor filter was placed in front of the window of the reaction cell.

Procedure

Since the vapor pressure of sulfolane at room temperature is low ($\sim$ 0.02 Torr) [8], the photolysis was carried out at 70 - 130 °C. The saturated vapor pressure of sulfolane at 110 °C is $\sim$ 2 Torr, and the range of sulfolane pressure covered in our experiments was 0.4 - 2 Torr. Since the pressure of sulfolane could not be measured directly in our apparatus, it was calculated by introducing a measured amount of sulfolane into the reaction vessel of known volume. After introducing the reactants into the reaction vessel and evacuation, the reaction vessel was placed in a temperature-regulated oven, and irradiated with a low-pressure mercury lamp. The irradiation time was 5 min in the experiments without a foreign gas to keep the conversion to less than 10%, and 30 - 60 min in the presence of foreign gas.

The number of photons absorbed by mercury in the present system was determined by using the mercury-photosensitized reaction of N_2O (100 Torr of N_2O and 50 - 100 Torr of C_2H_6). The average amount of light absorbed by Hg vapor saturated at room temperature was 7.3×10^{16} photons/s.

Analysis

After each irradiation, the mixture of products was collected in a gas buret. For the analysis of SO_2 in the products, a measured amount of the product mixture was transferred into a solution of aqueous Na_2HgCl_4 and the amount of SO_2 was determined spectrophotometrically [9]. The remaining part of the product mixture was analyzed by g.l.c., using a 2 m column packed with 2% squalane alumina at 100 °C with N_2 as carrier gas. The amount of H_2 was determined with a thermal conductivity detector, and a flame ionization detector was used for hydrocarbon analysis.

Results

Reaction products

Analysis showed that the main reaction products were SO_2, H_2, C_2H_4, C_2H_2 and c-C_4H_8; the minor products were CH_4, C_2H_6, C_3H_8 and C_3H_6; and

TABLE 1

Yields of main reaction products (in μ mol)

Pressure of sulfolane (Torr)	c-C_4H_8	C_2H_4 (total)*	C_2H_2	H_2	SO_2 (obsd)	SO_2 (cald)
0.18	0.23	1.52	1.48	1.57	1.73	1.70
0.36	0.21	2.17	0.88	1.83	1.75	1.73
0.72	0.22	2.50	0.62	1.69	1.75	1.74
1.44	0.32	2.23	0.31	1.69	1.54	1.59

*See the text below for the meaning of "total".

n-C_4H_{10}, 1-C_4H_8 and CO were present only in trace amounts. Organic products other than the hydrocarbons mentioned were not investigated.

The amounts of the major products at 110 °C with 5 min irradiation are given in Table 1. In this experiment, the reaction vessel was saturated with Hg vapor at 0 °C, but in the other experiments described hereafter the reaction vessel was saturated with Hg vapor at room temperature. The amount of SO_2 determined spectrophotometrically was compared with the expected value calculated from the amounts of hydrocarbons, and it showed good agreement. The minor hydrocarbon products are assumed to be secondary products from ethylene through the addition of H atoms, which are presumed to be produced through abstraction by $Hg(^3P_1)$ from sulfolane. To estimate the amount of ethylene originally formed from sulfolane (called "total ethylene"), a correction was made by adding the amount of ethylene calculated from the minor hydrocarbons to the amount of ethylene determined by g.l.c. This correction amounts to $\sim$ 10% of the total ethylene. As will be discussed later, we assumed C_2H_2 and H_2 were formed via a molecular process from energy-rich ethylene, but the amount of H_2 found was in excess of that of C_2H_2, and the excess H_2 was probably produced through some hydrogen abstraction processes which may take place without desulfonylation.

The amounts of the major products increased almost linearly with irradiation time up to about 3 min, and after that the rates of formation decreased gradually. The decrease of rates of formation after about 3 min may be due to consumption of sulfolane and/or quenching of $Hg(^3P_1)$ and triplet sulfolane by the reaction products (Fig. 1).

It was confirmed that the pyrolysis of sulfolane at 110 °C is negligible. Although the light absorption of sulfolane at 253.7 nm was reported to be very small, its direct photolysis was examined with a quartz cell 10 cm in length and 5 cm in diameter. Irradiation for more than several hours at 110 °C did not give noticeable amounts of products.

Pressure dependence of the reaction rates

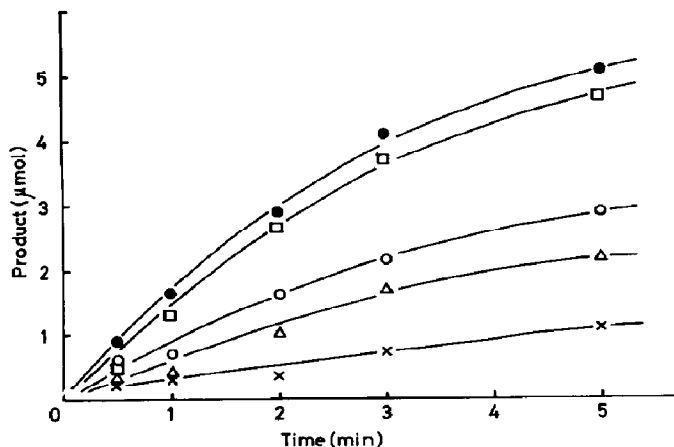Since the range of available sulfolane pressures is limited to 0.36 to 2.00

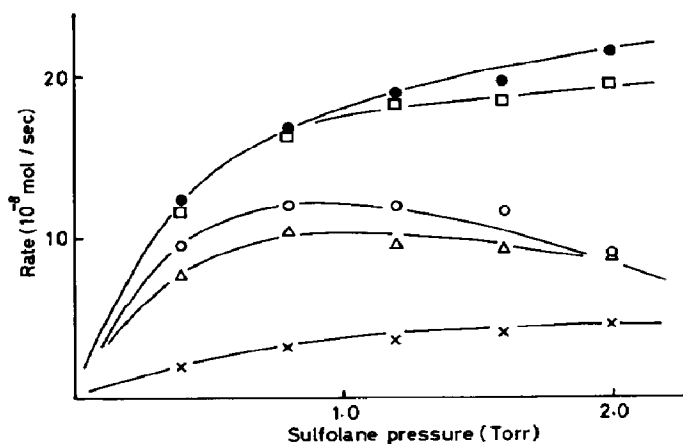Fig. 1. Product yields vs. irradiation time. Irradiation of sulfolane at 110 °C and 1.4 Torr. ●, Total C_2H_4; □, SO_2; ○, H_2; △, C_2H_2; ×, c-C_4H_8.

Fig. 2. Rate of product formation vs. pressure of sulfolane. ●, Total C_2H_4; □, SO_2; ○, H_2; △, C_2H_2; ×, c-C_4H_8.

Torr owing to its low vapor pressure, it may be questioned whether it is meaningful to discuss the pressure effect of sulfolane on the reaction rate. However, our investigation shows a clear pressure effect on the rates of production of the major products even in such a narrow pressure range. When the rates of product formation vs. pressure of sulfolane are plotted (Fig. 2), R_{SO_2} and $R_{c\text{-}C_4H_8}$ behave in a similar way, approaching constant values, while $R_{C_2H_2}$ and R_{H_2} show maxima at about 0.8 Torr. In the lower pressure region, the concentration of sulfolane may not be enough to quench the excited mercury atoms completely in comparison with the radiative lifetime of Hg ($^3P_1$), while at 2.0 Torr it may almost completely quench Hg($^3P_1$). In order to make clear the pressure dependence of each product, we plotted $R_{C_2H_4}$, R_{H_2}, $R_{C_2H_2}$ and $R_{c\text{-}C_4H_8}$ normalized to R_{SO_2} vs. sulfolane pressure (Fig. 3). It will be seen that $R_{c\text{-}C_4H_8}/R_{SO_2}$ is independent of sulfolane pressure and that
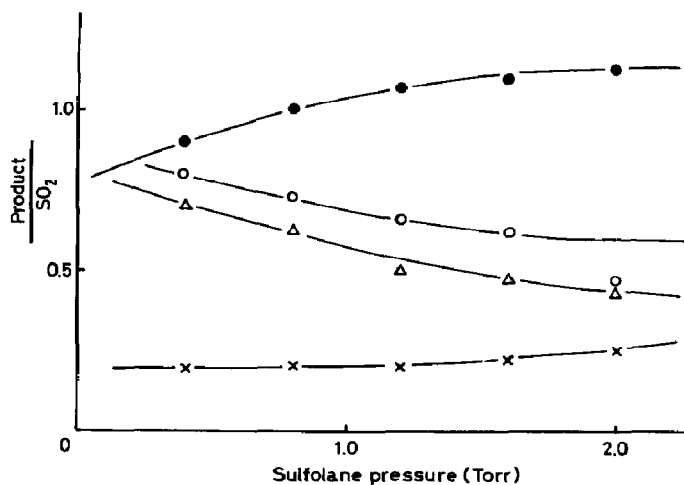
Fig. 3. Rate-ratio $R_{product}/R_{SO_2}$ vs. pressure of sulfolane. ●, Total C_2H_4; ○, H_2; △, C_2H_2; ×, c-C_4H_8.

$R_{C_2H_4}/R_{SO_2}$ and $R_{C_2H_2}/R_{SO_2}$ behave in the opposite way, as the increase of $R_{C_2H_4}$ compensates the decrease of $R_{C_2H_2}$. These results suggest that c-C_4H_8 is formed from triplet sulfolane almost independently of sulfolane pressure, while C_2H_2 and H_2 are produced through some form of energy-rich ethylene, which is easily susceptible to the quenching substance.

Effect of addition of nitric oxide and ethylene

In order to distinguish the molecular process from the radical process in the present reaction system, the effect of NO addition on the rates of product formation was investigated. Keeping the pressure of sulfolane at 0.36 Torr, NO at 0.33 or 0.68 Torr was added. The addition of NO suppressed remarkably the formation of CH_4, C_2H_6, C_3H_8 and C_3H_6. It is also observed that NO addition reduced the amount of SO_2, C_2H_4, C_2H_2, c-C_4H_8 and H_2 to some

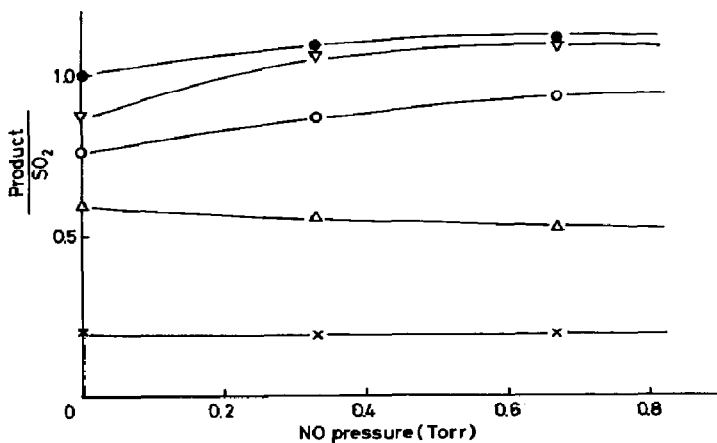Fig. 4. Rate-ratio $R_{product}/R_{SO_2}$ vs. pressure of NO. ●, Total C_2H_4; ▽, C_2H_4; ○, H_2; △, C_2H_2; ×, c-C_4H_8.

extent. This reduction is probably due to the competing quenching of Hg ($^3P_1$) by NO. As Fig. 4 shows, if we take the ratio $R_{c\text{-}C_4H_8}/R_{SO_2}$, it is independent of the pressure of NO. The behavior of $R_{C_2H_4}$ and $R_{C_2H_2}$ is similar to that in the case of the pressure effect of sulfolane. While $R_{C_2H_2}$ decreases slightly with increase of pressure of NO, R_{H_2} increases. Although there is no conclusive explanation for this increase, the excited NO formed by the quenching of Hg($^3P_1$) may abstract an H atom from sulfolane to give more hydrogen. Another possible process to give H_2 is by the catalytic action of NO to form H_2 according to the reaction:

$$H + NO \rightarrow HNO \xrightarrow{\text{H}} H_2 + NO.$$

In order to scavenge H atoms, ethylene was added intentionally to the reaction system. In Table 2, the ratio of yield of H_2 to that of C_2H_2 in relation to the pressure of added C_2H_4 is shown, indicating that C_2H_4 scavenges H atoms and that the ratio (H_2/C_2H_2) approaches unity with the addition of C_2H_4. Further, it is observed that the amounts of the minor hydrocarbon products increase with the addition of C_2H_4. Since the ratio (H_2/C_2H_2) approaches but does not fall below unity, it may be concluded that energy-rich ethylene primarily produces molecular hydrogen and C_2H_2 in equal amounts*.

TABLE 2

Effect of addition of ethylene

Pressure of sulfolane, 0.36 Torr; 110 °C; 5 min irradiation

C_2H_4 (Torr)	0	0.34	0.60
H_2/C_2H_2	1.23	1.15	1.01

Experiment in the presence of benzene

In order to see whether benzene-photosensitized decomposition of sulfolane takes place or not, a mixture of 2 Torr of sulfolane and 5.8 or 10.4 Torr of benzene was irradiated at 110 °C for 30 min with the low-pressure mercury lamp. Actually no products were found by g.l.c., and it is concluded that sulfolane does not decompose with benzene-photosensitization.

Effect of reaction temperature

The effect of reaction temperature on the rate of formation of products was investigated between 70 and 130 °C. Although the experimental points are rather scattered, no appreciable variation is observed.

Effect of addition of foreign gases on the reaction rates

The mercury-photosensitized reaction of sulfolane was carried out in

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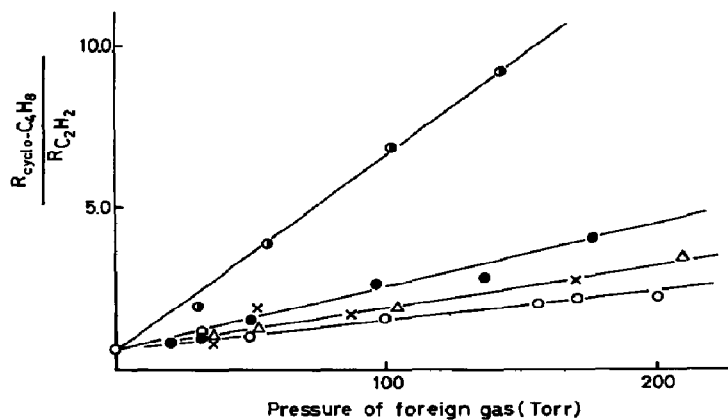*It may be noted that no formation of C_2H_2 has been observed in the direct photolysis of cyclopentanone.

Fig. 5. Rate-ratio $R_{c\text{-}C_4H_8}/R_{C_2H_2}$ vs. pressure of foreign gas. ⊕, SF_6; ●, Xe; △, Ar; ×, He; ○, N_2.

the presence of SF_6, Xe, Ar, He or N_2. Since the experiments in the absence of foreign gas described above were carried out under pressures of sulfolane below 2 Torr, the decomposition of triplet sulfolane may take place from relatively high vibrationally excited states. In the experiments on the addition of foreign gases, the absolute amounts of products could not be determined, since the products as collected were diluted with a large amount of foreign gas. In addition, the reaction seems to proceed much more slowly than that in the absence of foreign gas, probably owing to the quenching of $Hg(^3P_1)$ by the foreign gas, so the irradiation time was extended to 30 - 60 min, and the relative ratios, $R_{c\text{-}C_4H_8}/R_{C_2H_2}$ and $(R_{C_2H_4} + R_{C_2H_2})/2R_{c\text{-}C_4H_8}$ were determined by g.l.c. By adding 20 - 250 Torr of foreign gas to 2 Torr of sulfolane at 110 °C, we observed the pressure effect on the rate of photolysis of sulfolane. In Fig. 6 $R_{c\text{-}C_4H_8}/R_{C_2H_2}$ vs. the pressure of foreign gas is plotted. The detailed discussion of these results will be given later.
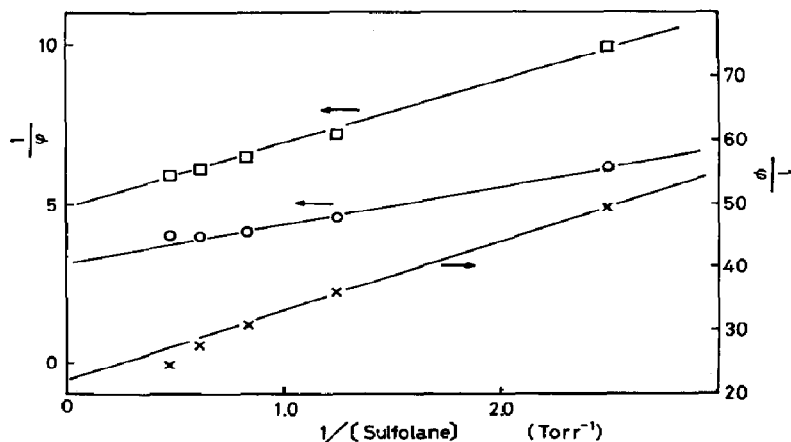

Fig. 6. $1/\Phi$ vs. pressure of sulfolane. □, $1/\Phi_{SO_2}$; ○, $1/(\Phi_{C_2H_4} + \Phi_{C_2H_2})$; ×, $1/\Phi_{c\text{-}C_4H_8}$.

Mercury-photosensitized reaction of sulfolane-2,2,5,5-d_4

In order to elucidate the detailed reaction mode yielding C_2H_4 from triplet sulfolane, mercury-photosensitized reaction of sulfolane-2,2,5,5-d_4 was carried out with 5 min irradiation at 0.7 Torr and 110 °C. The proce·dures of the experiment were just the same as described above. Among the reaction products, the mixture of ethylene and deuterated ethylenes was separated from other hydrocarbons by passing the reaction mixture through a trap cooled to —140 °C. The isotope distribution of deuterated ethylene in the reaction products was determined by mass spectroscopy (m.s.) (electron energy of 70 eV). The m.s. was corrected by subtracting the contribution of ^{13}C to higher mass peaks and the fragment contribution to lower peaks, but the isotope effect on the m.s. sensitivity and fragmentation was neglected. The result is shown in Table 3, and it is concluded that the decomposition of triplet sulfolane proceeds through the fission of the C_3–C_4 bond but not of the C_2–C_3 and C_4–C_5 bonds*, since ethylene-d_2 is the major product, and the formation of ethylene-d_4 is negligible. The formation of some ethylene-d_3 may be explained, considering the presence of 10% of sulfolane-d_5 in the reactant mixture. However, the formation of C_2H_3D and C_2H_4 could not be explained by considering the isotopic composition of the original sulfolane. Although we have no definite conclusion, a hydrogen shift in the original sulfolane due to Hg($^3P_1$) might be a possible explanation.
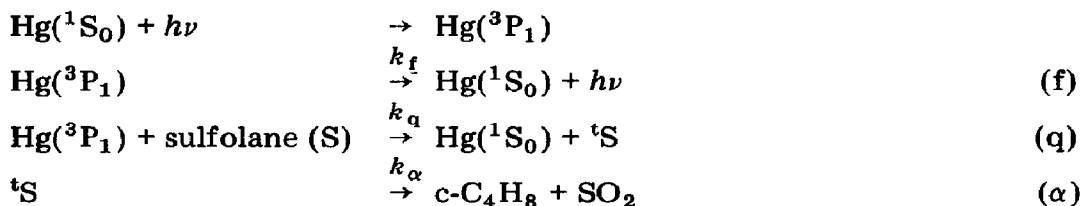
TABLE 3

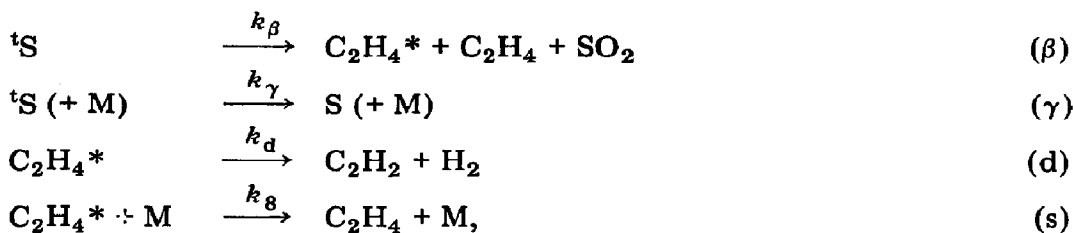Isotope distribution of deuterated ethylenes (mol %)

m/e	28	29	30	31	32
	C_2H_4	C_2H_3D	$C_2H_2D_2$	C_2HD_3	C_2D_4
%	11.1	19.6	51.8	15.6	1.9

Discussion

As with many mercury-photosensitized reactions of organic compounds which have π-electron systems, the reaction of sulfolane with Hg($^3P_1$) may be represented by the following scheme:

$$Hg(^1S_0) + h\nu \quad \rightarrow \quad Hg(^3P_1)$$

$$Hg(^3P_1) \quad \overset{k_f}{\rightarrow} \quad Hg(^1S_0) + h\nu \qquad (f)$$

$$Hg(^3P_1) + \text{sulfolane (S)} \quad \overset{k_q}{\rightarrow} \quad Hg(^1S_0) + {}^tS \qquad (q)$$

$${}^tS \quad \overset{k_\alpha}{\rightarrow} \quad \text{c-}C_4H_8 + SO_2 \qquad (\alpha)$$

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*It is interesting that fission of the C_3–C_4 bond is observed as well in the direct photolysis of cyclopentanone-2,2,5,5-d_4 [1] as in the electron impact of sulfolane-2,2,5,5-d_4.

$$^tS \xrightarrow{k_\beta} C_2H_4^* + C_2H_4 + SO_2 \tag{β}$$

$$^tS\ (+\ M) \xrightarrow{k_\gamma} S\ (+\ M) \tag{γ}$$

$$C_2H_4^* \xrightarrow{k_d} C_2H_2 + H_2 \tag{d}$$

$$C_2H_4^* + M \xrightarrow{k_8} C_2H_4 + M, \tag{s}$$

where ^tS designates triplet sulfolane, and $C_2H_4^*$ is energy-rich ethylene. The formation of triplet sulfolane is assumed because of its large quenching cross-section to excited mercury and the spin-conservation rule. Although the triplet energy level of sulfolane is not known, it seems to be higher than the triplet level of benzene, since sulfolane does not decompose with benzene photosensitization. A further detailed discussion on the branching ratio of process (α) and (β) and the formation of energy-rich ethylene will be given later. Process (γ) may be either a unimolecular radiationless transition or a bimolecular quenching, but in our experiments it is not possible to distinguish which. However, since the range of pressure in the experiments in the absence of foreign gas is very narrow, we may treat it as pseudo-unimolecular. The values of k_α, k_β and k_γ may not be the same in either the absence or the presence of foreign gas, but in the experiments in the presence of a large amount of foreign gas we could not determine these rate constants and quantum yields owing to the difficulty of measuring the absolute yields of products.

On the basis of the above reaction scheme, the following rate equations are derived, assuming steady-state conditions for $Hg(^3P_1)$ and triplet sulfolane:

$$\frac{1}{\Phi_{SO_2}} = \left(\frac{k_f}{k_q}\right)\left(1 + \frac{k_\alpha}{k_\alpha + k_\beta}\right)\frac{1}{[S]} + \left(1 + \frac{k_\gamma}{k_\alpha + k_\beta}\right) \tag{1}$$

$$\frac{1}{\Phi_{c\text{-}C_4H_8}} = \left(\frac{k_\alpha + k_\beta + k_\gamma}{k_\alpha}\right)\left(\frac{k_f}{k_q\ [S]} + 1\right) \tag{2}$$

$$\frac{1}{\Phi_{C_2H_4^*}} = \left(\frac{k_\alpha + k_\beta + k_\gamma}{k_\beta}\right)\left(\frac{k_f}{k_q\ [S]} + 1\right), \tag{3}$$

where [S] is the concentration of sulfolane. Figure 7 shows that these equations are satisfied, and a limiting value for Φ_{SO_2} is found to be 0.21, and for Φ_γ, 0.79, if we disregard other reactions such as hydrogen abstraction from sulfolane with $Hg(^3P_1)$. In addition, the value, k_f/k_q is found to be $1.58 \times 10^{-5}\ M^{-1}$ from the slope and intercept of the plot in Fig. 7. Separately we found the value of k_q by Cvetanović's N_2O technique to be $2.0 \times 10^{11}\ M^{-1}$ s^{-1} (cross-section 31.8 Å^2), which gives $3.2 \times 10^6\ s^{-1}$ for k_f. The value of k_f determined by this method is not the true radiative decay constant of Hg ($^3P_1$), since the effect of radiation imprisonment is not taken into account, but it seems to be of a reasonable order of magnitude compared with the re-
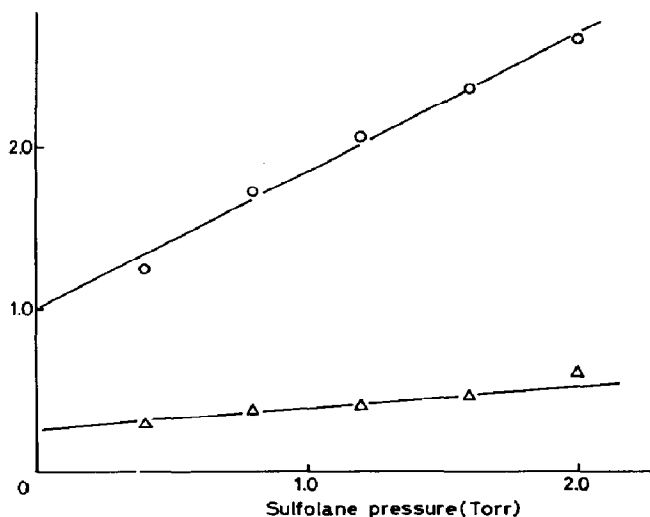
Fig. 7. Rate-ratios $R_{C_2H_4}/R_{C_2H_2}$ and $R_{c\text{-}C_4H_8}/R_{C_2H_2}$ vs. pressure of sulfolane. O, $R_{C_2H_4}/R_{C_2H_2}$; $\triangle$, $R_{c\text{-}C_4H_8}/R_{C_2H_2}$.

ported value of the radiative decay constant, 9×10^6 s^{-1}.

In the above reaction scheme, it is assumed that the energy-rich ethylene either decomposes to give C_2H_2 and H_2 or is stabilized by collision with a quencher (either sulfolane of foreign gas). Again assuming the steady state condition for the energy-rich ethylene, the following rate equations are derived:

$$R_{C_2H_4}/R_{C_2H_2} = 1 + 2 (k_s/k_d) [S] \tag{4}$$

$$R_{c\text{-}C_4H_8}/R_{C_2H_2} = (k_\alpha/k_\beta) (1 + (k_s/k_d) [S]) \tag{5}$$

Combining these equations, eqn. (6) is also derived:

$$(R_{C_2H_4} + R_{C_2H_2})/R_{c\text{-}C_4H_8} = 2(k_\beta/k_\alpha) \tag{6}$$

Figure 8 shows that these relationships are well satisfied, and k_s/k_d and k_α/k_β are determined from the slope and intercept as follows:

$$k_s/k_d = 1.1 \times 10^4 \ M^{-1} \qquad \text{and} \qquad k_\alpha/k_\beta = 0.27$$

In Fig. 8 it can be seen that $R_{C_2H_4}/R_{C_2H_2}$ extrapolated to zero pressure of sulfolane is unity, indicating that the energy-rich ethylene and normal ethylene are produced in equal amounts from triplet sulfolane. From the values $\Phi_{SO_2} = \Phi_\alpha + \Phi_\beta = 0.21$ and $k_\alpha/k_\beta = 0.27$, we find the quantum yields $\Phi_{c\text{-}C_4H_8}$ and $\Phi_{C_2H_4}$* to be 0.04 and 0.17 respectively.

For the case of the presence of a foreign gas, slightly modified rate equations are derived. The foreign gas is competing with sulfolane to quench $Hg(^3P_1)$ and triplet sulfolane, but these quenching effects are cancelled, if we take the rate ratios:

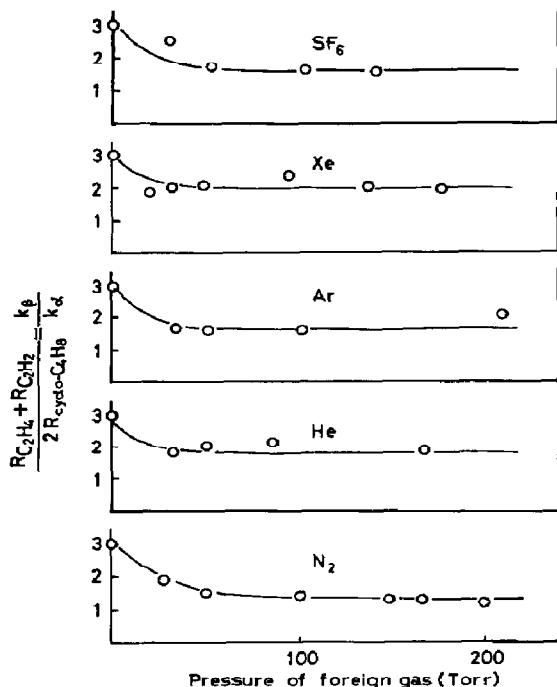$$(R_{c\text{-}C_4H_8}/R_{C_2H_2}) = (k_\alpha/k_\beta) (1 + (^Sk_s/k_d) [S] + (^Mk_s/k_d) [M] \tag{7}$$

Fig. 8. Rate-ratio $(R_{C_2H_4} + R_{C_2H_2})/2R_{c\text{-}C_4H_8}$ vs. pressure of foreign gas.

$$(R_{C_2H_4} + R_{C_2H_2})/R_{c\text{-}C_4H_8} = 2(k_\beta/k_\alpha), \tag{8}$$

where ^Sk_s is the quenching rate constant of sulfolane for energy-rich ethylene, and ^Mk_s is that of the foreign gas. Since [S] is kept constant at 2 Torr in the present experiments, plots of $R_{c\text{-}C_4H_8}/R_{C_2H_4}$ vs. [M] should be linear, and $(R_{C_2H_4} + R_{C_2H_2})/R_{c\text{-}C_4H_8}$ should be independent of pressure. It is shown in Fig. 6 that the linear relationship is well satisfied, and in Fig. 8 it is shown that k_β/k_α is constant in the presence of rare gases, while in the presence of SF_6 or N_2 k_β/k_α increases slightly in the low-pressure region, reaching 3.7 in the absence of foreign gas. In Table 4, the values of k_s/k_d determined from
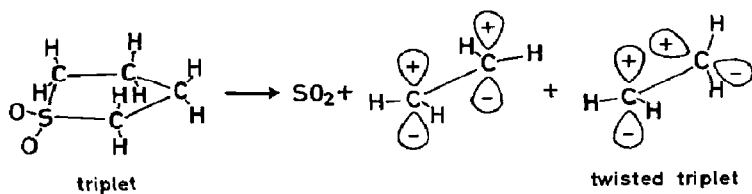

Fig. 9. Schematic model of the decomposition of triplet sulfolane yielding twisted ethylene.

the slopes of the plots in Fig. 6, the relative cross-sections normalized to that of SF_6, and k_β/k_α are listed. The order of the relative cross-sections, sulfolane

TABLE 4

Rate-constant ratios and relative cross-sections

	Sulfolane	SF_6	N_2	Xe	Ar	He
$k_q/k_d \times 10^{-3}\ M^{-1}$	11	1.77	0.22	0.71	0.41	0.43
Relative cross-section*	6.1	(1.00)	0.09	0.40	0.19	0.09
k_β/k_α	3.7	1.6	1.3	2.0	1.7	1.9

*Assumed k_d is the same for all quenchers.

$> SF_6 > Xe > Ar > He$ is reasonable except for that of N_2 which seems to have a rather small cross-section. There seems to be some difference in the magnitude of k_β/k_α depending on the quenching gas and its pressure. We may tentatively interpret this difference by assuming that the vibrationally highly excited triplet sulfolane (in the absence of foreign gas) gives a larger value of k_β/k_α than triplet sulfolane cooled by a quencher, but further investigations will be necessary to reach a conclusion.

Some further detailed discussion on the reaction mechanism from the energetic point of view.

Though we have no knowledge of the exact amount of energy transferred to sulfolane from $Hg(^3P_1)$, it may be useful to evaluate the amount of exothermicity for the possible reaction paths, assuming that all the $Hg(^3P_1)$ energy is transferred to sulfolane. To do this, it is necessary to know the heat of formation of sulfolane. Although the heat of formation of sulfolane itself has not yet been reported, Mackle *et al.* [10] reported the heat of formation of sulfolane to be —61.1 kcal/mol. Combining this value with the heat of hydrogenation of sulfolene [assuming that this heat is the same as that of cyclopentene (—27 kcal/mol)], we obtain —88 kcal/mol for the heat of formation of sulfolane. With this value, the following heats of reactions may be calculated as shown in Table 5, and it is to be noted that these reactions are exothermic.

Among these reactions, reaction (I) seems to be less likely. If we would assume that all the energy (89.5 kcal/mol) is retained in $c-C_4H_8$, hot $c-C_4H_8$ must be easily susceptible to decomposition yielding C_2H_4 and energy-rich ethylene (or C_2H_2 and H_2). However, $R_{c-C_4H_8}/R_{SO_2}$ and $R_{c-C_4H_8}/(R_{C_2H_4} + R_{C_2H_2})$ are both independent of the pressure of sulfolane and other quenchers. If C_2H_4 (and C_2H_2) were produced through hot $c-C_4H_8$, $R_{C_2H_4} + R_{C_2H_2}$ would decrease and $R_{c-C_4H_8}$ would increase with increase of the pressure of quencher. Further, in the experiment on sulfolane-2,2,5,5-d_4, we would expect the formation of C_2H_4, $C_2H_2D_2$ and C_2D_4 in the ratio 1:2:1 from hot cyclobutene-1,1,4,4-d_4. But our experimental finding is that $C_2H_2D_2$ is the major product and the formation of C_2D_4 is negligible.
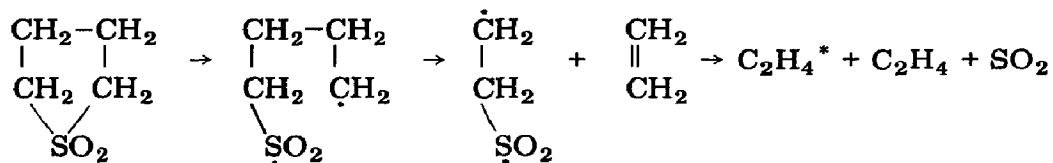
TABLE 5

Maximum values for heat of reaction of $Hg(^3P_1)$ with sulfolane

Reaction		$-\Delta H$ (kcal/mol)
(I)	$Hg(^3P_1) + \text{sulfolane} \rightarrow c\text{-}C_4H_8 + SO_2$	~ 90
(II)	$\rightarrow c\text{-}C_4H_8 + SO_2 \text{ (triplet)}$	~ 15
(III)	$\rightarrow \cdot CH_2CH_2CH_2CH_2\cdot + SO_2$	$5 >$
(IV)	$\rightarrow 2C_2H_4 + SO_2$	~ 71
(V)	$\rightarrow C_2H_4 + C_2H_4{}^* \text{ (twisted triplet)} + SO_2$	~ 25
(VI)	$\rightarrow C_2H_4 + C_2H_2 + H_2 + SO_2$	~ 29

Therefore, for the formation of $c\text{-}C_4H_8$, reaction (V) is the most probable one, since the excess energy of $c\text{-}C_4H_8$ is very small, and the spin conservation rule is preserved. Our finding that $R_{c\text{-}C_4H_8}$ is insensitive to the pressure of quencher is consistent with this. It is difficult to distinguish reaction (II) from reaction (III), but at any rate the formation of a tetramethylene biradical with a long lifetime is less likely, since no scavenging effect of NO is observed on $R_{c\text{-}C_4H_8}$.

For the formation of energy-rich ethylene, we consider reaction (V). However, the actual process is probably not the simultaneous (or concerted) fissions of three bonds, and the following successive fissions may be more realistic:

$$\begin{array}{ccccccc} CH_2-CH_2 & & CH_2-CH_2 & & \dot{C}H_2 & CH_2 & \\ | \quad | & \rightarrow & | \quad | & \rightarrow & | & + \quad \| & \rightarrow C_2H_4{}^* + C_2H_4 + SO_2 \\ CH_2 \; CH_2 & & CH_2 \; \dot{C}H_2 & & CH_2 & CH_2 & \\ \diagdown \diagup & & \diagdown & & \diagdown & & \\ SO_2 & & \dot{S}O_2 & & \dot{S}O_2 & & \end{array}$$

The fact that $R_{C_2H_4}$ and $R_{C_2H_2}$ are equal at zero pressure of quencher (sulfolane) indicates that one molecule of ethylene is different from another in structure in the sense of chemical or electronic state. Although we have no direct evidence on this point, the initial formation of twisted ethylene may be most probable from energetic and spin-conservation considerations.

For the formation of C_2H_2 from energy-rich ethylene, already many studies [11 - 17] have been reported in the various reaction systems, and usually twisted ethylene and ethylidene radicals are proposed as the intermediate, and the comparisons of the experimental values of k_d with the calculated one by Kassel model or RRKM model have been presented. In the present case, if the excess energy retained in triplet ethylene is assumed to be 25 kcal/mol as shown in Table 5, this is almost the threshold value for forming acetylene from energy-rich ethylene. Nevertheless, the experimentally deter-

mined value of k_s/k_d shown in Table 4 seems to be low enough as compared with the values reported in the cases of other compounds, indicating that k_d in the present case is fairly large in spite of the relatively low excess energy retained in energy-rich ethylene.

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References

1 R. Srinivasan, in J. N. Pitts, G. S. Hammond and W. A. Noyes (eds.), Advances in Photochemistry, Vol. 1, Wiley–Interscience, New York, 1963, p. 83.
2 S. Tsunashima, O. Ohsawa, C. Takahashi and S. Sato, Bull. Chem. Soc. Japan, 46 (1973) 83, and references cited therein.
3 Y. Odaira, K. Yamaji and S. Tsutsumi, Bull. Chem. Soc. Japan, 37 (1964) 1410.
4 M. P. Cava, R. H. Schlessinger and J. P. Van Meter, J. Am. Chem. Soc., 86 (1964) 3173.
5 J. Saltiel and L. Metts, J. Am. Chem. Soc., 89 (1967) 2232.
6 J. Schurz and H. Stübchen, Z. Elektrochem., 61 (1957) 754.
7 D. S. Weinberg, C. Stafford and M. W. Scoggins, Tetrahedron, 24 (1968) 5409.
8 R. L. Benoit and G. Choux, Can. J. Chem., 46 (1968) 3215.
9 P. W. West and G. C. Gaeke, Analyt. Chem., 28 (1956) 1816.
10 H. Mackle and P. A. G. O'Hare, Trans. Faraday Soc., 57 (1961) 1873.
11 A. B. Callear and R. J. Cvetanović, J. Chem. Phys., 24 (1956) 873.
12 R. F. Hampson, Jr. and J. R. McNesby, J. Chem. Phys., 43 (1965) 3592.
13 T. Terao, S. Hirokami, S. Sato and R. J. Cvetanović, Can. J. Chem., 44 (1966) 2173.
14 H. E. Hunzicker, J. Chem. Phys., 50 (1969) 1288.
15 K. Obi, Y. Ogata, H. Akimoto and I. Tanaka, J. Chem. Phys., 55 (1971) 3822.
16 Y. Ogata, K. Obi, H. Akimoto and I. Tanaka, Bull. Chem. Soc. Japan, 44 (1971) 2671.
17 H. Akimoto, K. Obi and I. Tanaka, ibid., 46 (1973) 2267.