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# The Reactions of Propylene-1,3,3,3-$d_4$ Photosenitized by Hg($^3P_1$), Cd($^3P_1$), and Benzene-$h_6$ and -$d_6$

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A comparative study has been made of the reactions of *cis*- and *trans*-propylene-1,3,3,3-$d_4$ photosensitized by benzene-$h_6$ and -$d_6$ and by Hg($^3P_1$) at room temperature and by Cd($^3P_1$) at 275°C. The main reaction observed in every photosensitization was a *cis-trans* isomerization; no isomerization to propylene-2,3,3,3-$d_4$ was observed under the conditions employed. This is in marked contrast to the isomerization of ethylene-$d_2$. The ratio of *cis*- to *trans*-propylene-1,3,3,3-$d_4$ after prolonged irradiation was unity. The decomposition observed in the mercury photosensitization was also studied in detail; its quantum yield was less than one-tenth that of the *cis-trans* isomerization. The material balance between the decrease in the reactant and the amount of the products was well preserved, but the energy balance between the absorbed photons and the quantum yield of products was not preserved at pressures below 150 Torr. A possible mechanism is discussed.

*cis*- or *trans*-Dideuteroethylene, when photosensitized by benzene or Cd($^3P_1$), undergoes two types of reactions: (i) *cis-trans* isomerization, and (ii) hydrogen-atom scrambling, *i. e.*, the formation of 1,1-dideuteroethylene.[1-3] Since the $\pi$ electronic structure of propylene is similar to that of ethylene, it seemed interesting to study whether or not propylene undergoes reactions similar to those of ethylene.

On the other hand, in the study of the reaction of 2-butene photosensitized by Hg($^3P_1$) we have found that the balance between the absorbed quanta and the sum of the quantum yields of products is not preserved at pressures below 150 Torr.[4] In

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[1] T. Terao, S. Hirokami, S. Sato and R. J. Cvetanović, *Can. J. Chem.*, **44**, 2173 (1966).

[2] S. Hirokami and S. Sato, *ibid.*, **45**, 3181 (1967).

[3] S. Tsunashima, S. Hirokami and S. Sato, *ibid.*, **46**, 995 (1968).

[4] S. Tsunashima and S. Sato, This Bulletin, **41**, 284 (1968).

other words, a part of the energy absorbed by mercury atoms does not seem to contribute to the chemical reactions occurring in the system over a wide range of pressure. We tentatively explained this observation in terms of the formation of vibrationally-excited states of the reactant.

With these prospects in mind, a study of the reactions of partially-deuterated propylene-1,3,3,3-$d_4$, was made by using mercury and cadmium atoms and benzene-$h_6$ and -$d_6$ as the photosensitizers.

## Experimental

*trans*- and *cis*-Propylene-1,3,3,3-$d_4$ were synthesized from methylacetylene-$d_4$ by a method previously described.[5] Methylacetylene-$d_4$ was obtained by means of a reaction between magnesium carbide and heavy water.[6] Methylacetylene was separated from other compounds by gas chromatography using a column packed with dimethylsulforane-on-celite. The mass-spectrometric analysis showed the isotopic impurities in the synthesized methylacetylene-$d_4$ to amount of less than 5%. Research-grade *cis*-2-butene and propylene-$h_6$ supplied by the Takachiho Trading Co. were used after bulb-to-bulb distillations. According to the gas-chromatographic analysis, the impurities in *cis*-2-butene amounted to less than 0.5%, and those in propylene, to less than 0.1%. Benzene-$h_6$ and -$d_6$ were both of a spectrograde; they were supplied by the Merck Co. The mass-spectrometric analysis of benzene-$d_6$ showed that the isotopic impurities amounted to less than 2%.

The light sources and the apparatus used were similar to those reported on in previous papers. The reaction vessels used for the mercury photosensitization had volumes of 52.3 m*l* (a), 25.4 m*l* (b), and 9.4 m*l* (c).

The isomerization products were analyzed with a Perkin-Elmer 125 double-beam grating infrared spectrometer. The absorption peak at 983 $cm^{-1}$ was assigned to *trans*-, the peak at 785 $cm^{-1}$, to *cis*-propylene-1,3,3,3-$d_4$, and the peak at 912 $cm^{-1}$, to propylene-2,3,3,3-$d_4$.[*1]

In the mercury photosensitization, various products were obtained. They were analyzed as follows. After each run, the reaction products were transferred into a trap at the temperature of liquid nitrogen and non-condensables were collected in a gas buret by means of a Toepler pump. After the amount had been measured, the gas was analyzed by means of a mass-spectrometer. For the condensed part, a cold trap at −120°C was used to separate the reaction products from the reactant, propylene. The amount of propylene remaining was measured volumetrically, and the products condensed at −120°C were identified and measured with a gas chromatograph equipped with dimethylsulpholane (10 m long), dioctylphthalate columns (2 m long), and a flame-ionization detector.

The light intensity absorbed by benzene-$h_6$ and -$d_6$ was estimated by using the benzene-$h_6$ or -$d_6$-photosensitized *cis-trans* isomerization of *cis*-2-butene.[7] In the mercury photosensitization, the light intensity of the 2537 Å resonance line used for the reaction was estimated from the amount of hydrogen produced in the mercury-photosensitized decomposition of ethylene at 45 Torr, assuming the quantum yield to be 0.203.[8] The absorbed light intensity of the cadmium-resonance line at 3261 Å was estimated by using the cadmium-photosensitized *cis-trans* isomerization of *cis*-2-butene.[4]

## Results

**Photosensitizations by Benzene-$h_6$ and -$d_6$.** By the photosensitization of benzene-$h_6$ or -$d_6$, the *cis-trans* isomerization of propylene-1,3,3,3-$d_4$ was observed to occur, but neither decomposition nor isomerization to propylene-2,3,3,3-$d_4$ was observed. Table 1 summarizes the results. After prolonged irradiation, a 1 : 1 ratio of *cis*- to *trans*-propylene-1,3,3,3-$d_4$ was obtained, but not even a trace of

TABLE 1. ISOMERIZATION OF *cis*-PROPYLENE-1,3,3,3-$d_4$ PHOTOSENSITIZED BY BENZENE-$h_6$ AND -$d_6$

| Benzene Torr | Propylene Torr | Benzene triplet* μ mol | Products % | |
|---|---|---|---|---|
| | | | *cis* | *trans* |
| | | Benzene-$h_6$ | | |
| 0.22 | 0.40 | 109 | 49.3 | 50.7 |
| 0.50 | 0.55 | 11.6 | 86.1 | 13.9 |
| 0.50 | 0.74 | 13.9 | 87.2 | 12.9 |
| 0.50 | 0.97 | 21.8 | 85.2 | 14.8 |
| 0.50 | 1.75 | 43.6 | 82.3 | 17.7 |
| 0.50 | 5.13 | 11.2 | 85.4 | 14.6 |
| 0.50 | 6.19 | 11.2 | 87.6 | 12.4 |
| 0.50 | 8.01 | 11.2 | 88.5 | 11.5 |
| 3.8 | 6.08 | 12.3 | 85.3 | 14.7 |
| 3.8 | 8.58 | 16.8 | 84.9 | 15.1 |
| 3.8 | 14.5 | 39.8 | 79.8 | 20.1 |
| | | Benzene-$d_6$ | | |
| 0.22 | 0.40 | 79.8 | 50.0 | 50.0 |
| 0.50 | 0.55 | 15.4 | 82.3 | 17.7 |
| 0.50 | 0.74 | 17.4 | 83.5 | 16.5 |
| 0.50 | 0.97 | 26.1 | 79.3 | 20.7 |
| 0.50 | 1.73 | 44.4 | 77.8 | 22.2 |
| 0.50 | 4.07 | 8.74 | 82.9 | 17.1 |
| 0.50 | 4.92 | 9.90 | 85.2 | 14.8 |
| 0.50 | 6.19 | 9.53 | 88.0 | 12.0 |
| 0.50 | 7.74 | 9.67 | 89.2 | 10.8 |

* Estimated by the isomerization of *cis*-2-butene. This value is related to the amount of photons absorbed by benzene as follows: [Benzene triplet] = [Photons absorbed] × $\phi_T$.
$\phi_T$ is the quantum yield of benzene triplet.[7,10]

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[5] B. S. Rabinovitch and F. S. Looney, *J. Amer. Chem. Soc.*, **75**, 2652 (1953).

[6] Y. Hatano, S. Shida and S. Sato, This Bulletin, **41**, 1120 (1968).

[*1] The infrared absorption spectrum of this compound was kindly supplied by the Byron Trading Co.

[7] W. A. Noyes, Jr. and D. A. Harter, *J. Chem. Phys.*, **46**, 674 (1967).

[8] B. DeB. Darwent, *ibid.*, **19**, 258 (1951).

propylene-2,3,3,3-$d_4$ was observed. The quantum yield of the formation of propylene-2,3,3,3-$d_4$ must be less than one-thousandth at the pressures employed, if it occurs at all.

**Cadmium Photosensitization.** The products obtained in the reaction of propylene-1,3,3,3-$d_4$ photosensitized by cadmium were *cis-trans* isomers, plus small amounts of propane and probably $C_6$-hydrocarbons, whose elution times on a gas chromatograph were almost equal to those of $C_6$ hydrocarbons. After prolonged irradiation (72 $\mu$Einstein, the pressure of the reactant being 23 Torr), equal amounts of *cis-* and *trans*-propylenes were obtained, but propylene-2,3,3,3-$d_4$ was again not observed.

**Mercury Photosensitization.** Mercury-photosentitized reactions were studied with *cis*-propylene-1,3,3,3-$d_4$ and propylene-$h_6$. Even in the mercury photosensitization, the formation of propylene-2,3,3,3-$d_4$ could not be observed. Table 2 summarizes the mol% of *trans-* and *cis*-propylene-$d_4$ observed after the mercury-photosensitized reaction.

In this photosensitization, the decomposition process cannot be ignored. Table 3 shows the pressure dependence of the quantum yields of the decomposition products observed when propylene-$h_6$ and *cis*-propylene-$d_4$ were used as the reactants. Obviously, at pressures above 20 Torr the decomposition products consist mainly of $C_6$-hydrocarbons. In order to check the material balance, the amount of propylene-$h_6$ consumed in the mercury photosensitization was measured over a wide range of pressures. The results are shown in Fig. 1, which also includes the plots of the quantum yields of the $C_6$-hydrocarbons and non-condensable gas formed. Obviously, the quantum yield of the consumption of propylene is about twice that of the formation of $C_6$-hydrocarbons.

TABLE 2. $Hg(^3P_1)$ PHOTOSENSITIZED *cis-trans* ISOMERIZATION OF *cis*-PROPYLENE-1,3,3,3-$d_4$

| *cis*-Propylene Torr | Photons absorbed $\mu$Einstein | $C_3H_2D_4$ % | | Reaction cell |
|---|---|---|---|---|
| | | *trans* | *cis* | |
| 48.1 | 97.3 | 50.4 | 49.6 | c |
| 100.9 | 94.2 | 39.9 | 60.1 | c |
| 103.2 | 64.4 | 30.8 | 69.2 | c |
| 8.9 | 17.4 | 13.4 | 86.6 | a |
| 10.5 | 4.4 | 2.6 | 97.4 | a |
| 11.0 | 17.4 | 12.4 | 87.6 | a |
| 12.6 | 4.4 | 2.8 | 97.2 | a |
| 12.7 | 17.4 | 10.8 | 89.2 | a |
| 13.9 | 17.4 | 11.2 | 88.8 | a |
| 14.1 | 4.4 | 2.4 | 97.6 | a |
| 15.5 | 4.4 | 2.6 | 97.4 | a |
| 16.4 | 17.4 | 10.2 | 89.8 | a |
| 17.4 | 4.4 | 2.5 | 97.5 | a |
| 18.1 | 17.4 | 9.1 | 90.9 | a |
| 25.3 | 18.2 | 13.9 | 86.1 | b |
| 29.3 | 19.6 | 13.9 | 86.1 | b |
| 33.1 | 19.6 | 12.4 | 87.6 | b |
| 36.3 | 19.8 | 10.9 | 89.1 | b |
| 45.7 | 39.1 | 19.0 | 81.0 | b |
| 53.4 | 36.3 | 14.5 | 85.5 | b |
| 68.6 | 43.0 | 17.1 | 82.9 | b |
| 74.0 | 39.6 | 12.6 | 87.4 | b |
| 98.5 | 21.4 | 15.3 | 84.7 | c |
| 142.8 | 37.4 | 18.0 | 82.0 | c |
| 178.2 | 43.9 | 17.3 | 82.7 | c |
| 200.8 | 42.8 | 16.8 | 83.2 | c |
| 229.1 | 46.0 | 16.1 | 83.9 | c |

In order to discuss the energy balance between the absorbed quanta and the quantum yields of the products, the $C_6$-hydrocarbons from the re-

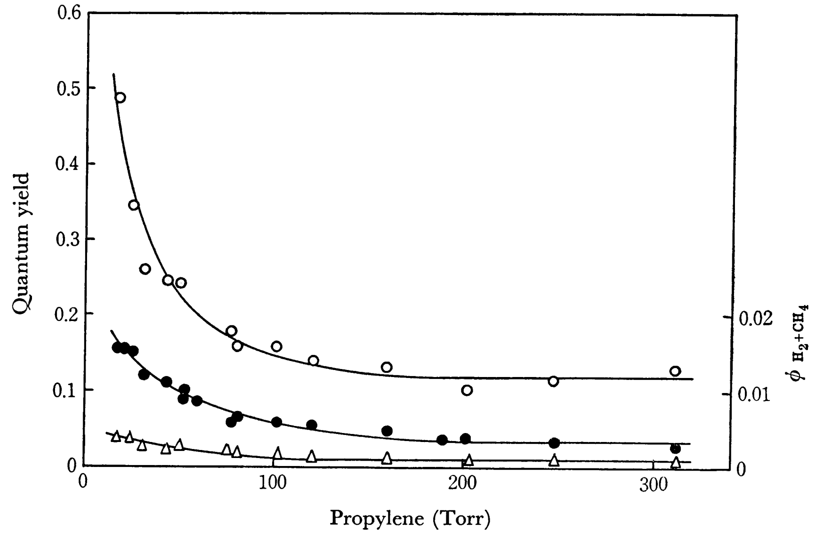


Fig. 1. Pressure dependence of the quantum yields of $C_6$-hydrocarbons (●), non-condensable gas (△) and propylene-$h_6$ consumed (○).

TABLE 3. PRESSURE DEPENDENCE OF QUANTUM YIELDS OF PRODUCTS IN THE MERCURY PHOTOSENSITIZATION

| | $C_3H_6$ | | | $C_3H_2D_4$ | |
|---|---|---|---|---|---|
| Reactant pressure (Torr) | 21.0 | 53.0 | 80.2 | 19.3 | 82.0 |
| Quantum Yields $\times 10^3$ | | | | | |
| Hydrogen and Methane | 7.1 | 4.9 | 3.0 | — | — |
| Ethane and Ethylene | 13.0 | 7.3 | 3.7 | 3.0 | 0.6 |
| Propane | 19.8 | 11.7 | 8.6 | 2.6 | 1.3 |
| Acetylene | 6.7 | 4.3 | 1.3 | 4.0 | 0.9 |
| Butene-1 | 9.3 | 5.7 | 2.6 | 1.8 | 0.5 |
| 2,3-Dimethylbutane | 26.1 | 16.0 | 10.6 | 5.0 | 2.4 |
| 4-Methylpentene-1 | 83.4 | 52.0 | 28.7 | 15.1 | 7.2 |
| Hexene-1 | 4.8 | 3.2 | 3.2 | 0.7 | 0.5 |
| 1,5-Hexadiene | 41.6 | 29.0 | 19.8 | 6.9 | 3.4 |
| Material Balance $\phi(\Delta$ propylene$) \times 10^3$ | | | | | |
| Calculated from | | | | | |
| Products | 357 | 228 | 137 | | |
| Observed | 380 | 240 | 160 | | |

TABLE 4. QUANTUM YIELD OF $C_6$-HYDROCARBONS PRODUCED IN THE MERCURY PHOTOSENSITIZED DECOMPOSTION OF *cis*-PROPYLENE-$d_4$

| Propylene Torr | Photons absorbed $\mu$Einstein | Quantum yield $\phi(C_6) \times 10^2$ | Reaction cell |
|---|---|---|---|
| 10.3 | 6.27 | 4.7 | b |
| 15.2 | 12.5 | 3.8 | b |
| 19.3 | 6.6 | 2.8 | c |
| 27.2 | 18.8 | 1.9 | b |
| 29.2 | 5.9 | 2.5 | c |
| 50.9 | 10.4 | 1.4 | c |
| 51.5 | 25.1 | 1.6 | b |
| 76.4 | 14.8 | 1.4 | c |
| 82.0 | 15.8 | 1.4 | c |
| 100.9 | 20.0 | 1.3 | c |
| 141.4 | 21.6 | 0.9 | c |
| 198.4 | 38.5 | 0.8 | c |

action of *cis*-propylene-$d_4$ were also measure. The results are listed in Table 4. The pressure dependence of the quantum yield is very similar to that obtained with propylene-$h_6$ in Fig. 1. However, the absolute value is about a quarter that obtained with propylene-$h_6$. This is probably due to the isotope effect in the initial process of the mercury-photosensitized reaction.

## Discussion

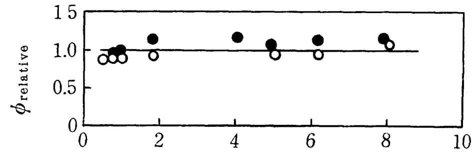
**Isomerization of Propylene-1,3,3,3-d$_4$.** The *cis-trans* isomerization of *cis*-propylene-$d_4$ may be visualized as follows:

$$cis\text{-}CD_3CH{=}CDH + S^* \longrightarrow P^* + S$$
$$P^* + M \longrightarrow 1/2\, trans + 1/2\, cis + M$$

Here, S and S* represent the ground state and the excited triplet state of a photosensitizer respectively. P* is an excited state of propylene, probably the lowest triplet. M is the third body for the stabilization. In the case of *cis*-ethylene-$d_2$, the state corresponding to P* further isomerizes to the second excited state, which is a precursor of 1,1-dideuteroethylene, but in the present case this process is ignored because the formation of propylene-2,3,3,3-$d_4$ was not observed in any photosensitized reaction performed. To estimate the initial quantum yield of the isomerization, the following equation has to be applied to the data because the reverse reaction from *trans*- to *cis*-isomer is always included in a finite conversion:

$$\phi_{\mathrm{iso}} = \frac{[\mathrm{C}]+[\mathrm{T}]}{2It} \ln \frac{[\mathrm{C}]+[\mathrm{T}]}{[\mathrm{C}]-[\mathrm{T}]} \qquad \text{(I)}$$

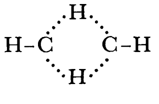
The derivation of this equation has already been shown in a previous paper.[9] Here, $\phi_{\mathrm{iso}}$ is the initial quantum yield of isomerization. It is the light quanta absorbed by a photosensitizer, and the brackets show the concentrations of *cis*- and *trans*-isomers after the reaction. Thus, the relative quantum yields of isomerizations photosensitized by benzene-$h_6$ and -$d_6$ are calculated to be as is shown in Fig. 2. Although the data are scattered, it may be said that the quantum yield of the *cis-trans* isomerization of *cis*-propylene-$d_4$ is independent of the pressure of the reactant above a few Torr. This trend has previously been observed in the isomerization of 2-butenes.[10]



*cis*-Propylene-$d_4$ (Torr)

Fig. 2. Relative quantum yield of *cis-trans* isomerization of propylene-1,3,3,3-$d_4$ photosensitized by benzene-$h_6$ (○) and benzene-$d_6$ (●).

As has been stated in the previous section, the formation of propylene-2,3,3,3-$d_4$ was not observed in any photosensitization, while this type of isomerization is important in the reaction of ethylene-$d_2$. The reason for this discrepancy is not clear, but a speculation may be offered. If the hydrogen-atom scrambling observed in the reaction of ethylene occurs through the formation of a structurally-symmetric intermediate such as



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[9] S. Tsunashima and S. Sato, This Bulletin, **42**, 329 (1969).

[10] M. Tanaka, K. Kato and S. Sato, *ibid.*, **39**, 1423 (1966).

then the substitution of a methyl radical for a hydrogen atom may disturb the formation of this type of intermediate. This structure for the hydrogen-atom scrambling state was suggested by Whalley years ago,[11] but it obviously needs more deliberate theoretical cansideration.

**Decomposition of Propylene.** An appreciable decomposition of propylene was observed only in the mercury photosensitization. The reaction mechanism has already been discussed by many investigators.[12–15] When propylene-1,3,3,3-d$_4$ is the reactant, the mechanism may be described as follows:

$$CD_3CH{=}CDH^* \longrightarrow D + \dot{C}D_2CH{=}CDH \qquad (1)$$

$$\searrow \dot{C}D_3 + \dot{C}H{=}CDH \qquad (2)$$

$$CD_3CH{=}CDH^* + M \longrightarrow 1/2\,trans + 1/2\,cis \qquad (3)$$

Here, CD$_3$CH=CDH* is the excited state of the propylene produced by the mercury photosensitization. This is probably the lowest triplet state. Reference to Tables 2 and 3 makes it obvious that the process (3) is the most important at pressures higher than 10 Torr and that the process (1) is preferable the process (2), since many more C$_3$ and C$_6$ hydrocarbons than C$_1$, C$_2$ and C$_4$ hydrocarbons are produced. In order to estimate the quantum yields of the decomposition processes, the material balance between the consumed reactant and the observed products has to be checked. This calculation has been made regarding carbon atoms. The results are included in Table 3. Obviously, the material balance obtained is not too bad in any of the runs examined.

The formation of C$_6$ hydrocarbons may be described as follows (here, propylene-h$_6$ is used as the reactant to avoid complexity):

$$C_3H_6^* \longrightarrow H + C_3H_5 \qquad (1)$$

$$H + C_3H_6 \longrightarrow C_3H_7 \text{ (mainly } CH_3\dot{C}HCH_3) \qquad (4)$$

$$2C_3H_7 \longrightarrow \text{2,3-dimethyl butane} \qquad (5)$$

$$\searrow C_3H_8 + C_3H_6 \qquad (6)$$

$$C_3H_7 + C_3H_5 \longrightarrow \text{4-methyl pentene-1} \qquad (7)$$

$$\searrow 2C_3H_6 \qquad (8)$$

$$2C_3H_5 \longrightarrow \text{1,5-hexadiene} \qquad (9)$$

A small amount of 1-hexene may be formed in the reaction between C$_3$H$_5$ and CH$_3$CH$_2$CH$_2$. The formation of this radical is in competition with that of the isopropyl radical in the reaction (4). The formation of 1-butene may result from the reaction of C$_3$H$_5$ with the CH$_3$ produced in the reaction (2). If the mechanism is correct so far, the quantum yield of the reaction (1) may be calculated by the following relations:

$$\phi_{C\text{-}H} = (C_3H_5)$$

$$= \phi(C_6H_{12}) + 2\phi(C_6H_{10}) + \phi(C_4H_8) \qquad (II)$$

$$\phi_{C\text{-}H} = (C_3H_7)$$

$$= \phi(C_6H_{12}) + 2\phi(C_6H_{14}) + 2\phi(C_3H_8) \qquad (III)$$

Here, the contribution of the reaction (8) is ignored. The quantum yield of this reaction may be comparable to that of the reaction (7). The values calculated by the relations (II) and (III), therefore, are meaningful only in their order. The calculated values are summarized in Table 5, which obviously shows a strong isotope effect on the rupture of the C–H bond. The estimation of the quantum yield of the reaction (2) may be similar but the calculation was not carried out because a large experimental error was expected.

TABLE 5. ESTIMATION OF THE QUANTUM YIELD OF CARBON-HYDROGEN BOND RUPTURE

| Reactant pressure (Torr) | Propylene-h$_6$ | | | Propylene-d$_4$ | |
|---|---|---|---|---|---|
| | 21.0 | 53.0 | 80.2 | 19.3 | 82.0 |
| $\phi_{C\text{-}H}$ or $\phi_{C\text{-}D}$ (II)* | 0.18 | 0.12 | 0.07 | 0.03 | 0.015 |
| (III)* | 0.18 | 0.11 | 0.07 | 0.03 | 0.015 |

* Calculated by Eqs. (II) and (III).

**Energy Balance in the Mercury Photosensitization.** It was found in the mercury-photosensitized decomposition of propylene-h$_6$ that the amount of the reactant consumed was almost consistent with that of the products observed, and that a large part of the products were C$_6$-hydrocarbons. In the case of *cis*-propylene-1,3,3,3-d$_4$, we could not measure the amount of the reactant consumed because the amount of the reactant itself was small

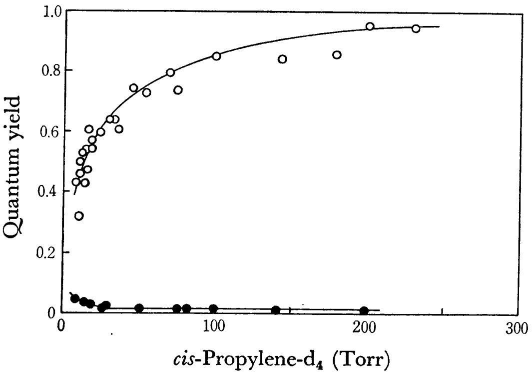

Fig. 3. Pressure dependence of the quantum yields of isomerization (○, 2$\phi_{iso}$) and C$_6$-hydrocarbons (●, $\phi_{C_6}$).

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[11] E. Whalley, *Can. J. Chem.*, **35**, 565 (1957).

[12] H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.*, **14**, 57 (1946).

[13] F. P. Lossing, D. G. H. Marden and J. B. Farmer, *Can. J. Chem.*, **34**, 701 (1956).

[14] M. Avrahami and P. Kebarle, *J. Phys. Chem.*, **67**, 354 (1963).

[15] C. A. Heller and A. S. Gordon, *J. Chem. Phys.*, **42**, 1262 (1965).

and we had to avoid a high conversion in order to estimate the quantum yield of isomerization. However, judging from the results obtained with propylene-$h_6$, the $C_6$-hydrocarbons obtained with *cis*-propylene-$d_4$ may form the main part of the decomposition products. Figure 3 shows the quantum yields of the *cis-trans* isomerization and of the formation of $C_6$-hydrocarbons in the reaction of *cis*-propylene-1,3,3,3-$d_4$ photosensitized by mercury. The quantum yield of the *cis-trans* isomerization was calculated by applying Eq. (I) to the data in Table 2. If all the photons absorbed by mercury atoms contribute to the reaction of the *cis-trans* isomerization or decomposition, the sum of the two quantum yields in Fig. 3 should be nearly equal to unity at any reactant pressure. Obviously, the sum deviates from unity with a decrease in the pressure of the reactant and approaches 0.5 at the pressure of 10 Torr. This trend has already been observed in the reaction of 2-butene photosensitized by mercury, where the quantum yield of decomposition was estimated from the formation of hydrogen.[4]

To explain this observation, we tentatively propose a mechanism including the formation of a vibrationally-excited state of olefins. The mechanism may be described as follows:

$$\mathrm{Hg}^* + cis\text{-}\mathrm{P} \longrightarrow \mathrm{HgP}^* \qquad (10)$$

$$\mathrm{HgP}^* \longrightarrow \begin{cases} \mathrm{Hg}+\mathrm{P}^* & (11)\\ \mathrm{Hg}+\mathrm{P}' & (12)\\ \mathrm{Hg}+\text{Decomposition} & (13) \end{cases}$$

$$\mathrm{HgP}^* + \mathrm{P} \xrightarrow{(\mathrm{HgP_2}^*)} \mathrm{Hg} + \mathrm{P}^* + \mathrm{P} \qquad (14)$$

Here, P* is the triplet state which is subject to the *cis-trans* isomerization and P′ is the vibrationally-excited state which does not isomerize. If the quantum yield of the process (12) is represented by $\phi_X$, its value may be approximated by the following relation:

$$\phi_X = 1 - (2\phi_{iso} + \phi_{C_6})$$

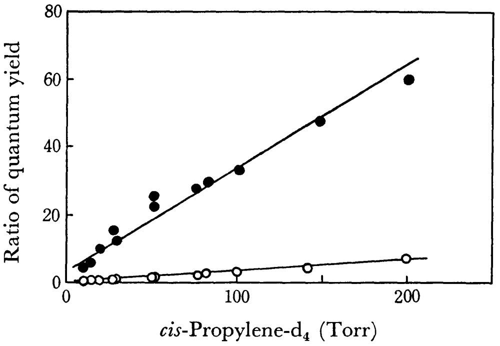

Fig. 4. Pressure dependences of the ratios, $\phi_{iso}/\phi_X$ (○) and $\phi_{iso}/\phi_{C_6}$ (●).

Figure 4 shows the pressure dependences of the ratios among these three quantum yields. Although the plots are scattered, it may be concluded that $\phi_{iso}/\phi_X$ and $\phi_{iso}/\phi_{C_6}$ are linearly dependent on the pressure. If so, and if the mechanism proposed above is correct, the contribution of the process (11) to the *cis-trans* isomerization should be small compared with that of the the process(14), because the linear relations for $\phi_{iso}/\phi_X$ and $\phi_{iso}/\phi_{C_6}$ have small intercepts at zero pressure. In other words, the main quenching process should occur through the formation of an unstable intermediate, $\mathrm{HgP_2}^*$, in the reaction of propylene photosensitized by mercury at pressures higher than 10 Torr. Obviously, further experiments and different approaches are needed to confirm this speculation.

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