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Reactions of *cis*- and *trans*-2-Butenes Photosensitized by $Hg(^3P_1)$ and $Cd(^3P_1)$

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A comparative study has been made of the reactions of *cis*- and *trans*-2-butenes photosensitized by mercury($^3P_1$) at room temperature and by cadmium($^3P_1$) at temperatures ranging from 275 to 350°C. In both cases, the main reaction was cis-trans isomerization. The initial quantum yield of isomerization was the same for the two butenes. The rate of decomposition was about 10^{-2} and 10^{-3} times less than that of isomerization in the Hg- and Cd-photosensitizations, respectively. The ratio of *trans*- to *cis*-2-butene after prolonged irradiation was unity and did not vary with pressure in the Cd-photosensitization, while in the Hg-photosensitization it increased with decreasing initial pressure. This is probably due to the difference in the rates of decomposition of *trans*- and *cis*-2-butenes. It was found that the pressure dependence of Hg-photosensitized *cis-trans* isomerization could not be explained in terms of the simple mechanism proposed before. A possible mechanism is discussed.

The rate of photosensitized isomerization of an olefin depends upon three factors; (1) the electronic state of the excited sensitizer molecule and its lifetime, (2) the mechanism of energy transfer from sensitizer to olefin, and (3) the reactivity of the excited olefin molecules. Recent studies have uncovered many interesting features of photosensitized isomerizations and have indicated the importance of the above factors in determining the rate of isomerization.

Photosensitized isomerization of 2-butenes in the gas phase has been investigated with mercury,[1,2] benzene[3] and several organic compounds[4] as sensitizers, but no report has appeared yet with cadmium. LeRoy and Steacie reported only on the decomposition of 2-butene in Cd-photosensitization.[5]

This paper presents a detailed study of the reactions of 2-butenes photosensitized by $Hg(^3P_1)$ and $Cd(^3P_1)$. Some of the results are obviously at variance with the data reported previously.

Experimental

cis- and *trans*-2-Butenes supplied by Takachiho-Shoji Co. were used after degassing at liquid nitrogen

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[1] R. J. Cvetanović, H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.*, **31**, 573 (1959).

[2] R. B. Cundall, F. J. Fletcher and D. G. Milne, *Trans. Faraday Soc.*, **57**, 1692 (1961).

[3] S. Sato, K. Kikuchi and M. Tanaka, *J. Chem. Phys.*, **39**, 239 (1963); M. Tanaka, T. Terao and S. Sato, This Bulletin, **38**, 1645 (1965); M. Tanaka, K. Kato and S. Sato, *ibid.*, **39**, 1423 (1966); R. B. Cundall, F. J. Fletcher and D. G. Milne, *Trans. Faraday Soc.*, **61**, 1146 (1965).

[4] R. B. Cundall, "Progress in Reaction Kinetics," Vol. 2, ed. by G. Porter, Pergamon Press, Oxford (1964); D. Phillips, *J. Phys. Chem.*, **71**, 1839 (1967).

[5] D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.*, **10**, 683 (1942).

temperature. Major impurities observed by gas-chromatography were *trans-cis* isomers, the amounts being at most below 0.5%. *trans*-2-Butene-d_8 was synthesized from butadiene-$d_6$6) and was purified by gas-chromatography. The isotopic purity of *trans*-2-butene-d_8 was determined to be at least above 98%. Special grade nitrogen, nitrous oxide and sulfur hexafluoride supplied by Takachiho-Shoji Co. were used without further purification. Six 9's pure cadmium stick was used as supplied by Soekawa Chemical Co.

Quartz reaction cells were cylindrical (5 cm in diameter, 8, 5 and 3 cm long) and contained a drop of mercury or a few small pieces of cadmium.

Light sources were spiral low pressure mercury discharge lamps (filled with 4 mm Ne) and a cadmium discharge lamp of the same type (filled with 2 mm Ar).

To eliminate the $^1S_0$-$^1P_1$ resonance line, a Toshiba UV-25 filter which cuts off below 2000 Å or a Toshiba UV-29 filter which cuts off below 2500 Å, was inserted between the light source and the reaction cell.

For cadmium-photosensitization, the light source and the reaction cell were placed separately in two electric furnaces controlled by Toshiba Thermister Temperature Controllers to within ±2°C and ±1°C, respectively.

After each run, materials were transferred to a trap at liquid nitrogen temperature. The non-condensables were analyzed and measured with a combination of Toepler pump, gas buret and furnace (*ca.* 260°C) packed with cuprous oxide. The condensables were analyzed by gas-chromatography. The columns used were packed with a celite-dimethylsulpholane mixture (30 m long, supplied by Shimadzu Co.) and with activated alumina containing tailing reducer (7 m long, supplied by Nishio Kogyo Co.).

The isotopic distribution of hydrogen was determined by mass-spectroscopy.

In the experiments using mercury-photosensitization, the light intensity of the 2537 Å resonance line was determined by the amount of hydrogen produced from 13 mmHg of ethylene, assuming the quantum yield of hydrogen to be 0.35.7)

Results

Cadmium-photosensitization. For cadmium photosensitization, it is necessary to elevate the temperature of the reaction cell in order to obtain a sufficiently high vapor pressure of cadmium. To check for the possibility of thermal isomerization of 2-butene, 10 mmHg of *cis*-2-butene was kept in the reaction cell at 350°C for two hours. However, after this period of time, neither isomerization nor decomposition products could be detected. After one hour irradiation of 9.8 mmHg of *cis*-2-butene at room temperature with a cadmium lamp, likewise no reaction product was found. These results show that isomerization of 2-butene is not effected by radiation of the 3261 Å resonance line since the 2288 Å line is filtered out and that the light source used is not contaminated by mercury lines.

In the presence of cadmium vapor, *cis*- or *trans*-2-butene were isomerized to *trans*- or *cis*-2-butene by the radiation from the cadmium lamp. The initial rates of isomerization were constant over the pressure range 2 to 100 mmHg. There was no

TABLE 1. PRODUCTS FROM THE CADMIUM-PHOTOSENSITIZATION
(Reaction cell, 166 m*l*; Initial pressure, 10 mmHg)

Temperature °C	Time min	Products μmol				
		H_2	CH_4	C_3H_6	*trans*-2-C_4H_8	*cis*-2-C_4H_8
cis-2-Butene						
275	5	—	—	—	1.9	37.0
	180	0.09	0.1	0.2	23.1	23.1
300	5	—	—	—	4.1	33.1
	180	0.13	0.5	1.0	20.6	19.7
325	3	—	—	—	3.45	34.5
	120	0.19	0.65	1.5	19.7	18.1
350	3	—	—	—	4.4	32.0
	120	0.17	1.1	1.7	18.1	16.5
trans-2-Butene						
275	5	—	—	—	37.1	2.0
	180	0.09	0.11	0.3	23.2	20.8
300	5	—	—	—	34.1	4.0
	180	0.13	0.5	0.9	20.4	19.5
325	3	—	—	—	34.8	3.5
	180	0.16	1.0	1.8	19.5	18.1
350	3	—	—	—	32.6	4.1
	120	0.17	1.0	1.8	16.7	15.9

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6) H. Hatano and S. Shida, *J. Chem. Phys.*, **46**, 4784 (1967).

7) B. DeB. Darwent, *ibid.*, **19**, 258 (1951).

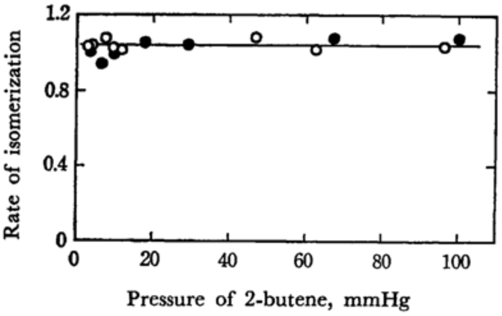

Fig. 1. Rate of isomerization at various pressures in the cadmium-photosensitization at 275°C. (○, cis → trans; ●, trans → cis)

difference in rate between two isomers (Fig. 1).

After prolonged irradiation, hydrogen, methane and propylene were observed. Their rates of formation were very small, *ca.* 10^{-3} of that of isomerization (Table 1).

After prolonged irradiation, the concentration ratio of *trans*- to *cis*-2-butene approached a value (unity) which was independent of the temperature (Table 2). The reduction in the total amount of 2-butene during an irradiation was negligibly small.

TABLE 2. THE RATIO OF *trans* TO *cis* AFTER PROLONGED IRRADIATION AT VARIOUS TEMPERATURES IN THE CADMIUM-PHOTOSENSITIZATION

Temperature, °C	Ratio of *trans* to *cis*
275	1.0_6
300	1.0_4
325	1.0_8
350	1.0_9

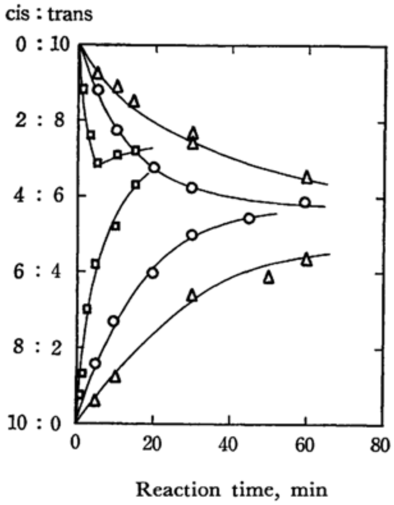

Fig. 2. Ratio of *trans*- to *cis*-2-butene in the mercury-photosensitization at room temperature. (Initial pressure: □, 1 mmHg; ○, 5 mmHg; △, 20 mmHg)

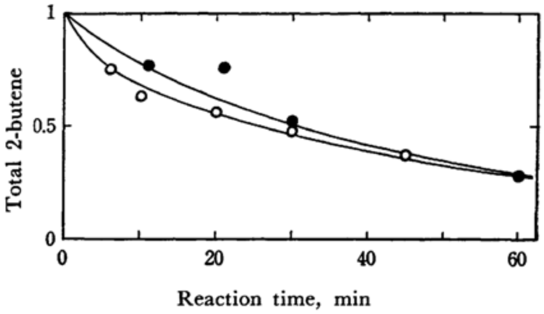

Fig. 3. Reduction of total amount of 2-butene in the mercury-photosensitization. (Initial pressure: 5.1 mmHg; ○: *cis*; ●: *trans*)

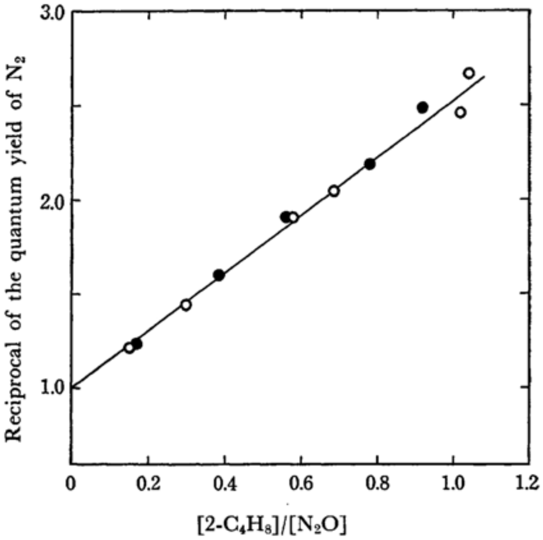

Fig. 4. Plots of the reciprocal of the quantum yield of nitrogen as a function of the ratio of the pressure of 2-butene to that of nitrous oxide. (○: *cis* → *trans*; ●: *trans* → *cis*)

Mercury-photosensitization. The products of the reaction of 2-butene photosensitized by Hg($^3P_1$) at room temperature were cis-trans isomer and small amounts of hydrogen, methane, propylene, *n*-butane and 1-butene. The rate of decomposition was *ca.* 10^{-2} of that of isomerization (Table 3).

The total amount of 2-butenes decreased with increasing reaction period and with decreasing initial pressure. After prolonged irradiation, the concentration ratio of *trans*- to *cis*-2-butene approached a constant value which was larger than unity and increased with decreasing pressure (Figs. 2 and 3).

Figure 4 shows the reciprocal of the quantum yield of nitrogen formation plotted against the ratio of the pressure of 2-butene to that of nitrous oxide, which is kept at 100 mmHg. The slope of the straight line in Fig. 4 obtained by the method of least squares was 1.6±0.1 for both butenes.

Table 3. Products from the mercury-photosensitization at room temperature
(Reaction cell, 166 m*l*)

Initial pressure mmHg	Reaction time min	Products μmol					
		H_2	CH_4	C_3H_6	*n*-C_4H_{10}	1-C_4H_8	*trans-cis* isomer
cis-2-Butene							
5.1	5	0.73	0.10	0.28	0.21	0.39	34.6
5.1	45	0.59	0.99	1.01	1.20	1.01	54.4
19.0	5	0.65	0.32	0.07	0.21	0.17	49.6
19.6	60	0.76	0.88	1.24	2.09	1.70	286
trans-2-Butene							
5.1	10	0.91	0.16	0.32	0.53	0.55	52.0
5.0	30	0.77	0.55	0.87	0.92	1.08	56.4
19.0	5	0.12	—	—	0.64	0.30	20.6
20.4	30	0.97	0.21	0.37	1.04	0.60	161

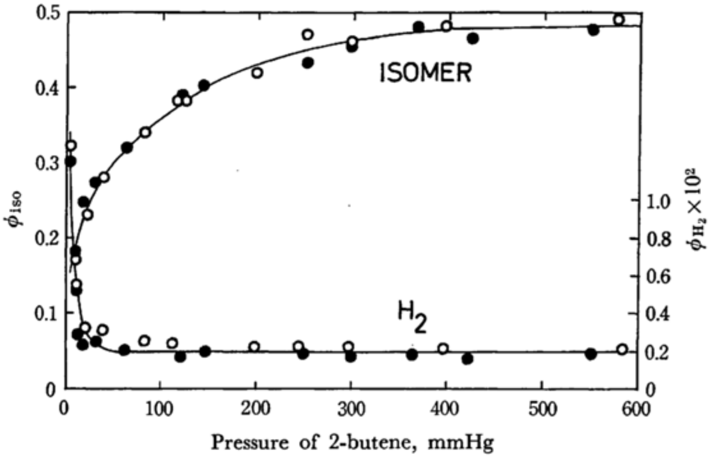

Fig. 5. Pressure dependence of the quantum yields of isomer and hydrogen formed in the mercury-photosensitization. (○, *cis*; ●, *trans*)

Assuming 17 Å^2 for the quenching cross section of nitrous oxide,[8] the quenching cross section of 2-butenes was estimated to be 30±2 Å^2.

The quantum yield of isomerization was identical for the two reactant isomers and increased with increasing initial pressure, approaching a value of about 0.5 above 300 mmHg (Fig. 5). The quantum

Table 4. Quantum yields of isomer with various light sources and intensities in the mercury-photosensitization
(Initial pressure: 20 mmHg)

Light source	Intensity Einstein/min	Reactant isomer	Quantum yield
A	3.55	*cis*	0.236
A	3.49	*trans*	0.224
A	3.94	*cis*	0.243
A	5.21	*cis*	0.214
B	11.6	*cis*	0.221
B	11.6	*trans*	0.221

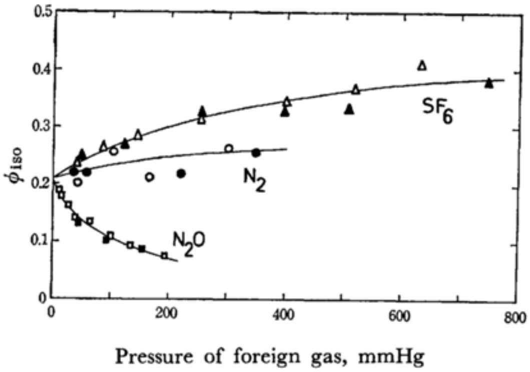

Fig. 6. Effects of foreign gases on the quantum yield of isomer formed in the mercury-photosensitization. (Initial pressure of 2-butene is 20 mmHg; △ ○ □, *cis*; ▲ ● ■, *trans*.)

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[8] A. J. Yarwood, O. P. Strausz and H. E. Gunning, *J. Chem. Phys.*, **41**, 1705 (1964).

yield of hydrogen decreased with increasing pressure and leveled off at 0.002 above 50 mmHg.

Table 4 shows the quantum yields of isomerization at 20 mmHg with various light intensities and lamps.

Figure 6 shows the effect of added gas; sulfur hexafluoride, nitrogen and nitrous oxide upon the quantum yield of isomerization at 20 mmHg of 2-butene. The quantum yield increased with sulfur hexafluoride, decreased with nitrous oxide and increased a little with nitrogen.

Discussion

Cadmium - photosensitization. *Decomposition Products.* The observed small amounts of decomposition products, hydrogen, methane and propylene, may be produced in the following mechanism;

$$\begin{array}{l} Cd^* + C_4H_8 \rightarrow CdH + C_4H_7 \\ CdH \rightarrow Cd + H \\ H + C_4H_8 \rightarrow H_2 + C_4H_7 \\ \qquad\qquad\;\; \rightarrow CH_3 + C_3H_6 \\ \qquad\qquad\;\; \rightarrow C_4H_9 \\ CH_3 + C_4H_8 \rightarrow CH_4 + C_4H_7 \end{array}$$

Here, Cd* stands for Cd($^3P_1$). C_4H_7 and C_4H_9 radicals may produce stable molecules by disproportionation or recombination. The total amount of these decomposition products is about 10^{-3} of that of isomerization which is one order of magnitude less than that in the case of mercury-photosensitization. This result may be due to the smaller energy available for decomposition in the case of Cd-photosensitization.

Mechanism of Isomerization. Neglecting the small amount of decomposition, the following mechanism may be considered for cis-trans isomerization of 2-butene;

$$Cd + h\nu \rightarrow Cd^* \tag{I}$$

$$Cd^* \rightarrow Cd + h\nu \tag{0}$$

$$Cd^* + T \rightarrow Cd + B^* \tag{1t}$$

$$Cd^* + C \rightarrow Cd + B^* \tag{1c}$$

$$B^* + M \rightarrow \alpha T + (1-\alpha)C + M \tag{2}$$

Here, T and C are *trans*- and *cis*-2-butenes, respectively. B* is the triplet state of 2-butene. α is the fraction of trans isomer formed from B*. The steady-state treatment gives the following relations;

$$\left.\begin{array}{l} d[C]/dt = I((1-\alpha)k_{1t}[T] - \alpha k_{1c}[C])/ \\ \qquad (k_0 + k_{1t}[T] + k_{1c}[C]) \\ d[T]/dt = I(\alpha k_{1c}[C] - (1-\alpha)k_{1t}[T])/ \\ \qquad (k_0 + k_{1t}[T] + k_{1c}[C]) \end{array}\right\} \quad (I)$$

TABLE 5. ISOTOPIC DISTRIBUTION OF HYDROGEN FORMED IN THE MERCURY-PHOTOSENSITIZATION OF 1 : 1 MIXTURE OF *trans*-2-BUTENE-d_0 AND -d_8

Initial pressure mmHg	H_2	HD %	D_2	$[HD]^2/[H_2][D_2]$
6.5	46.6	30.7	22.7	0.89
32.0	65.8	25.7	8.5	1.2

When reaction starts from pure isomers, the initial rates of isomerization should be expressed as follows;

$$\left.\begin{array}{l} R_{T\rightarrow C} = (1-\alpha)Ik_{1t}[T]/(k_0 + k_{1t}[T]) \\ R_{C\rightarrow T} = \alpha Ik_{1c}[C]/(k_0 + k_{1c}[C]) \end{array}\right\} \quad (II)$$

The relations, $k_0 \ll k_{1t}[T]$ or $k_{1c}[C]$ and $\alpha = 1-\alpha$, hold because, as Fig. 1 shows, $R_{T\rightarrow C} = R_{C\rightarrow T}$ and the rates of isomerization were not affected by the pressure change. Using the lifetime of Cd($^3P_1$) atom (2.4×10^{-6} sec9)) and quenching cross section (30.6 A^2)10), k_0 and $k_{1t}(=k_{1c})$ were calculated to be 4.2×10^5 sec^{-1} and 9.4×10^6 mm^{-1}sec^{-1}, respectively, *i. e.,* $k_0 \ll k_{1t}[T]$ or $k_{1c}[C]$ at the pressure over 1 mmHg. This is consistent with the present result.

The ratio of *trans*- to *cis*-2-butene obtained after prolonged irradiation ($[T]_\infty/[C]_\infty$) can be derived by setting $(d[C]/dt)_\infty = (d[T]/dt)_\infty = 0$ as follows,

$$[T]_\infty/[C]_\infty = \alpha k_{1c}/(1-\alpha)k_{1t} \tag{III}$$

Because $[T]_\infty/[C]_\infty$ is unity for all temperature ranges (Table 1), k_{1t} should be equal to k_{1c}, *i. e.,* the quenching cross section of *cis*-2-butene for Cd($^3P_1$) is equal to that of *trans*-2-butene.

Mercury - photosensitization. *Mechanism of Hydrogen Formation.* Hydrogen formation from an olefin molecule in Hg-photosensitization has been ascribed to the C–H bond cleavage of an excited olefin molecule.11) Accordingly, the quantum yield of hydrogen should approach zero at high pressures because of collisional deactivation. Figure 5, however, shows that the quantum yield of hydrogen does not approach zero even at 500 mmHg. This leads us to speculate that the following process plays a part in the mechanism;

$$\begin{array}{l} Hg(^3P_1) + C_4H_8 \rightarrow (Hg \cdots H \cdots C_4H_7)^* \\ \qquad \rightarrow Hg + H + C_4H_7 \end{array} \tag{3}$$

This kind of quenching process was proposed by Gunning *et al.*12) to account for the results of a study of the Hg-photosensitized decomposition of cyclohexene. Using the quantum yield of

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9) F. W. Byron, Jr., M. N. McDermott and R. Novick, *Phys. Rev.,* **134**, A 615 (1964).

10) E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.,* **11**, 164 (1943).

11) R. J. Cvetanović, "Progress in Reaction Kinetics," Vol. 2, ed. by G. Porter, Pergamon Press, Oxford (1964).

12) G. R. DeMare, O. P. Strausz and H. E. Gunning, *Can. J. Chem.,* **43**, 1329 (1965).

hydrogen at the pressure higher than 50 mmHg and the ratio of the rate of abstraction to that of addition (0.023 and 0.076 for *cis*- and *trans*-2-butene,[13] respectively), the quantum yields of the complex formation were estimated to be 0.09 and 0.025 for *cis*- and *trans*-2-butenes, respectively.

The quantum yield of hydrogen decreased with increasing initial pressure (Fig. 5). This behavior may be explained in terms of C–H bond cleavage of excited 2-butene molecules. Mixtures of *trans*-2-butene-d_0 and -d_8 were decomposed by Hg-photosensitization, in order to investigate the mechanism of hydrogen formation. The results are listed in Table 5. Obviously, the molecular elimination reaction occurred. Although the result seems to show the decrease of the molecular elimination with increasing pressure, further discussions can not be made because of the small rate of hydrogen formation.

The Ratio of trans- to cis-2-Butene. As is shown in Figs. 2 and 3, the ratio $[T]_\infty/[C]_\infty$ increased with decreasing initial pressure and at the same time, some disappearance of total 2-butene was observed. Possible explanations for this observation are as follows; (1) *trans*- and *cis*-2-butenes have different quenching cross sections for $Hg(^3P_1)$, (2) the ratio of *trans*- to *cis*-2-butene formed from the excited olefin molecule is not unity, (3) the ratio is affected by the disproportionation reaction of butyl and butenyl radicals and (4) the ratio is affected by the reduction of total 2-butene, *i. e.*, the rates of decomposition of cis and trans are different. The possibility (1) may be eliminated in view of the identical quenching cross sections found for the two isomers (Fig. 4). The possibility (2) can be omitted because the quantum yields of isomer do not differ for the two reactant isomers (Fig. 5). (3) may be ruled out because the amounts of the products of the disproportionation reaction such as 1-butene and *n*-butane are too small to explain the change of the ratio with pressure. The most probable explanation is the possibility (4), because the rate of decomposition of *cis*-2-butene is faster than that of *trans*-isomer (Fig. 3).

The Pressure Dependence of Quantum Yield of Isomer. Cundall *et al.*[2] assumed only one precursor for the isomerization of 2-butene photosensitized by $Hg(^3P_1)$ and derived the following relation.

$$P/R_{\rm iso} \propto P \qquad \text{(IV)}$$

Here, P and $R_{\rm iso}$ mean the initial pressure of 2-butene and the rate of isomerization, respectively. Equation (IV), however, explains the present results only approximately. We have attempted to establish a relationship which accounts for the pressure dependence of the quantum yield of isomerization. The following equation gives the relationship. The reaction mechanism which predicts the relationship will be discussed later.

$$\phi_{\rm iso} = \frac{b+c[{\rm P}]}{1+a[{\rm P}]}\,\frac{d[{\rm P}]}{1+d[{\rm P}]} \qquad \text{(V)}$$

Here, [P] is the initial pressure of 2-butene in mmHg and $\phi_{\rm iso}$ is the quantum yield of isomerization. The letters a, b, c and d are experimental parameters which are calculated to be 3×10^{-2} mmHg^{-1}, 0.1, 1.5×10^{-2} mmHg^{-1} and 1.3 mmHg^{-1}, respectively.

As seen in Fig. 5, the sum of the quantum yield of precursor for isomerization which is equal to $2\phi_{\rm iso}$ and that of C–H bond cleavage is almost unity above 300 mmHg. The quantum yield of C–H bond cleavage was estimated from that of hydrogen formed, using the ratio of the rate of abstraction to that of addition of a hydrogen atom.[13] In this estimation, the fraction of molecular elimination reaction was neglected, since it does not affect the present discussion. If the *cis-trans* isomerization and the cleavage of C–H bond are the only reactions induced by Hg-photosensitization, part of the absorbed light energy is lost at pressures below 300 mmHg of olefin. Incomplete quenching which can be estimated from the lifetime of $Hg(^3P_1)$ atoms (1.08×10^{-7} sec[14]) and from the quenching cross section of 2-butene (30 Å^2), is negligibly small above a pressure of 10 mmHg. A careful search was made for products other than *cis-trans* isomer, such as methyl cyclopropane (observed in the reaction of 1-butene photosensitized by $Hg(^3P_1)$[15]), cyclobutane, isobutene, 1-butene and C_8-compounds; but they were very small or not found at all. The disappearance of incident photons, therefore, remains unexplained.

The quantum yield of isomerization was unaffected by the light intensity. This suggests that the triplet-triplet anihilation of excited mercury atoms and of excited 2-butene, stepwise excitation processes and self reversal of the resonance line are negligible.

Cundall *et al.*[2] examined the effect of foreign gas on the isomerization and found that some compounds reduced the rate of isomerization with a competitive quenching for excited mercury atoms and some gave no effect because of the small quenching cross section of the foreign gas.

The effect of nitrous oxide, as is shown in Fig. 6, may be due to the competition for excited mercury atoms with 2-butene. The slight increase of the quantum yield of isomerization by adding nitrogen may be explained as the result of Lorentz

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[13] K. R. Jennings and R. J. Cvetanović, *J. Chem. Phys.*, **35**, 1233 (1961).

[14] A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," Cambridge University Press, London (1961).

[15] R. J. Cvetanović and L. C. Doyle, *J. Chem. Phys.*, **37**, 543 (1962).

broadening. The apparent increase of the quantum yield can be estimated by using Kang Yang's data[16] under the assumption that collision broadening of 2-butene is the same as that of ethylene. The estimated values are consistent with the experimental values within experimental error. Although nitrogen is known to be a quencher for the process, Hg($^3P_1 \rightarrow {}^3P_0$), the pressure used is still not high enough to induce the participation of Hg($^3P_0$) in this system.[11] The effect of sulfur hexafluoride appears to be complex. The quantum yield of isomerization increases with increasing pressure of added sulfur hexafluoride. Clearly, this effect cannot be associated with the removal of vibrational energy from the precursor since sulfur hexafluoride is known to be an effective quencher of vibrational energy.

With these data in mind, the following reaction mechanism is tentatively considered to explain the pressure dependence of the isomerization.

$$\mathrm{Hg} + h\nu \rightarrow \mathrm{Hg}^* \qquad (4)$$

$$\mathrm{Hg}^* \rightarrow \mathrm{Hg} + h\nu \qquad (5)$$

$$\mathrm{Hg}^* + \mathrm{C}\ (\text{or T}) \rightarrow \mathrm{HgC}^*\ (\text{or }\mathrm{HgT}^*) \qquad (6)$$

$$\mathrm{HgC}^*\ (\text{or }\mathrm{HgT}^*) \rightarrow \begin{cases} \mathrm{Hg} + \mathrm{B}^* & (7) \\ \mathrm{Hg} + \mathrm{C}^\dagger\ (\text{or }\mathrm{T}^\dagger) & (8) \end{cases}$$

$$\mathrm{HgC}^*\ (\text{or }\mathrm{HgT}^*) + \mathrm{M} \rightarrow \mathrm{Hg} + \mathrm{B}^* + \mathrm{M} \qquad (9)$$

$$\mathrm{B}^* \rightarrow (1/2)\mathrm{C} + (1/2)\mathrm{T} \qquad (10)$$

$$\mathrm{C}^\dagger\ (\text{or }\mathrm{T}^\dagger) \rightarrow \mathrm{C}\ (\text{or T}) \qquad (11)$$

Here, Hg*, C and T mean Hg($^3P_1$), *cis*- and *trans*-2-butene, respectively. B* may be the triplet state of 2-butene. HgC* or HgT* is a transient complex of *cis*- or *trans*-2-butene and excited mercury atom. $C^\dagger$ and $T^\dagger$ mean the vibrationally excited ground state of *cis*- and *trans*-2-butene which do not isomerize. The steady state treatment of the mechanism gives a relation of the type (V).

In this mechanism, the pressure dependence of the quantum yield of isomerization is explained by the competitive reactions, (7), (8) and (9). The effects of sulfur hexafluoride, nitrogen and nitrous oxide may be explained as follows; HgC* or HgT* is quenched efficiently by sulfur hexafluoride, but not by nitrogen and nitrous oxide. The reasoning of the mechanism, especially the reaction (8), must await further investigation.

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16) Kang Yang, *J. Am. Chem. Soc.*, **86**, 3941 (1964).