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The Zinc-Photosensitized Reaction of Propane

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The zinc-photosensitized reaction of propane has been studied at a wavelength of 307.6 nm, a temperature of 633 K and pressures from about 67 to 40000 Pa. The major products were hydrogen, methane, ethylene, and dimethylbutane, while minor products detected were propylene, isobutane, ethane, butane, and hexane. The yield of hydrogen fell off with time. The quantum yield calculated from the initial rates is about unity and almost independent of the propane pressure, while the quantum yield obtained at 20 min increased with increasing propane pressure and approached about unity at higher pressures. The methane/hydrogen ratio was always smaller than unity and was independent of the propane pressure. The yield of ethylene increased linearly with an increase in that of methane. It has been concluded that the decomposition of propane is initiated through a hydrogen atom abstraction by an excited zinc atom from both the primary and secondary hydrogen of propane. Possible mechanisms are discussed.

Although there has been a considerable amount of work carried out on the mercury-[1-6] and cadmium-photosensitized decomposition[7,8] of propane, almost no attention has been paid to the zinc-photosensitized reaction of alkanes.

In a previous paper,[9] a remarkable dependence of the quenching cross section of 307.6-nm zinc resonance line by alkanes on the C–H bond strength was reported. It was pointed out that the quenching cross section of a certain alkane can be estimated as the sum of the quenching cross section for each individual quenching site (C–H bond). These findings show that the excited zinc atoms attack all kinds of C–H bonds with efficiencies which depend on the bond strength.

Recently, we have further pointed out that the differences of activation energies for the quenching for primary, secondary, and tertiary C–H bond can be well interpreted in terms of a modified bond energy-bond order method by assuming the following reaction:[10]

$$Zn^* + RH \rightarrow Zn \cdots H \cdots R \rightarrow ZnH + R.$$

These results strongly suggest that hydrogen atom abstraction from alkanes by excited zinc atoms plays an important role in the quenching of $Zn(^3P_J)$.

We have examined the products from a zinc-photosensitized reaction of propane. Here, we report on the details of analytical results.

Experimental

A zinc-photosensitized reaction of propane was carried out in a cylindrical quartz cell. A spiral Pyrex zinc-discharge lamp filled with 2000-Pa argon was used as the source of the 307.6-nm resonance line. The cell and the lamp were inserted in an electric furnace kept at 360±2 °C in order to obtain a sufficient vapor pressure of zinc.

The zinc metal used was high-purity zinc (99.9999%) manufactured by the Osaka Asahi Metal Co. Research-grade propane (Tokyo Kasei K.K. 99.5%) was used after degassing at liquid-nitrogen temperature. The impurities detected by gas chromatography were ethane and propylene; the amount of propylene was below 0.1% of that of propane. Zinc metal was heated in vacumm and the zinc vapor was sealed into capillaries. The capillary and a known amount of propane were enclosed in the cell, and the capillary was broken just before each run.

Product analyses were carried out by fractionation at −196 °C, gas burette measures, and gas chromatography. The gases non-condensable at −196 °C (hydrogen and methane) were collected by a Toepler pump, and were analyzed by combustion over copper(II) oxide at 260 °C. The products which were condensable at −196 °C, were analyzed by gas chromatography, using a 6 m column of vz-7 (Gasukuro Kogyo Co., Ltd.) at 0 °C and a 2 m column of Gasukuro-pack 55 (Gasukuro Kogyo Co., Ltd.) at 30 °C.

The light intensity at 307.6 nm from the lamp was determined by diethyl ketone actinometry,[11] by assuming that the quantum yield of carbon monoxide production at 360 °C and 307.6 nm was unity, and by correcting for any contribution from photolysis by the 328.2- and 330.2-nm lines from the lamp.

Results and Discussion

The major products from the zinc-photosensitized decomposition of propane were hydrogen, methane, ethylene, and 2,3-dimethylbutane (DMB). The minor products detected were propylene, isobutane, ethane,

Table 1. Product Ratios in Zinc-Photosensitized Decomposition of Propane

P / Pa	H_2 / 10^{-6} mol	CH_4 / H_2	C_2H_4 / H_2	DMB / H_2	C_3H_6 / H_2	*iso*-C_4H_{10} / H_2	C_2H_6 / H_2	*n*-C_4H_{10} / H_2	*n*-C_6H_{14} / H_2
1790	0.653	0.58	0.59	0.10	0.08	0.05	0.04	0.01	0.01
6530	0.772	0.74	0.78	0.15	—	0.07	0.07	0.01	0.01
14300	0.843	0.65	0.70	0.21	—	0.09	0.03	0.03	—
25600	0.792	0.68	0.82	—	—	—	—	—	—
33300	1.049	0.72	0.80	—	—	—	—	—	—

butane, and hexane. Their yields were less than 10% of that of hydrogen (Table 1). Some products such as hydrogen, methane, and ethylene were detected when 6700-Pa propane was kept at 360 °C for 2 hours with zinc vapor in the dark; however, their yields were less than 2% of those from zinc-photosensitized reaction. Therefore, the thermal decomposition of propane and its reaction with zinc at 360 °C could be neglected.

The yields of hydrogen, methane, and ethylene increased linearly with the light intensity, while that of DMB showed a second-order dependence on the light intensity (Fig. 1). As Fig. 2 shows, the yield of hydrogen falls off with the reaction time, and the decrease in the yield is larger at lower pressures. This suggests that the influence of the products on hydrogen production is important at lower pressures.

The quantum yield of hydrogen production calculated from the initial rates is about unity and almost independent of the propane pressure, while the quantum yield obtained at a reaction time of 20 min increases asymptotically with increasing propane pressure to unity at high pressures (Fig. 3).

Appreciable amounts of methane are formed. The ratio of Φ_{CH_4}/Φ_{H_2} is almost independent of the propane pressure (Fig. 4). A roughly equal amount of ethylene to that of methane was produced. As Fig. 5 shows, the yield of ethylene increases linealy with an increase in methane.

As mentioned above, the quantum yield of hydrogen is about unity during the initial stage of the reaction and, as Fig. 3 shows, the quantum yield of hydrogen obtained at 20 min is close to unity at higher pressures and decreases with decreasing propane pressure. The experimental results obtained in the case of high propane pressures are very similar to those of mercury-

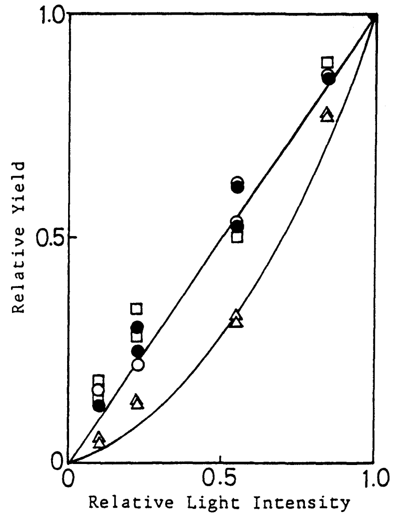

Fig. 1 Dependence of yields of hydrogen (●), methane (○), ethylene (□), and DMB (△) on light intensity in the zinc-photosensitized reaction of propane. ($P_{propane}$ is 30000 Pa and reaction time is 10min.)

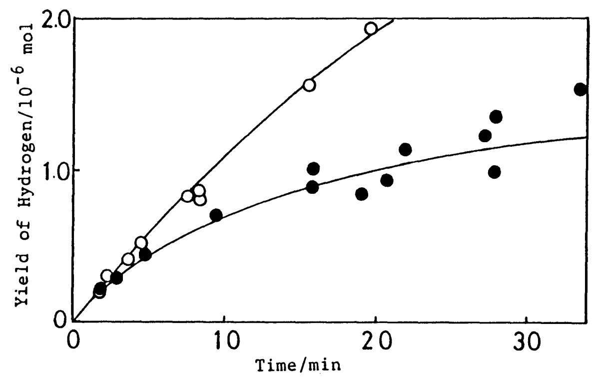

Fig. 2. Time dependence of yield of hydrogen. ○: 30000 Pa, ●: 1700 Pa.

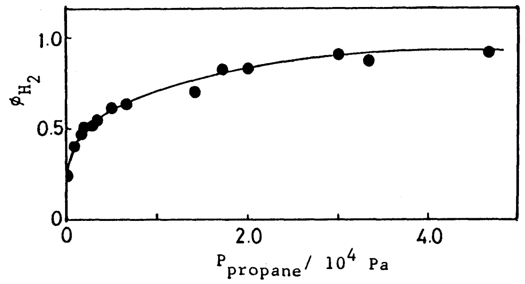

Fig. 3. Pressure dependence of quantum yield of hydrogen.

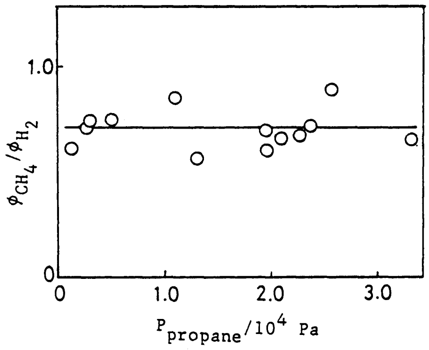

Fig. 4. Pressure dependence of Φ_{CH_4}/Φ_{H_2} ratio.

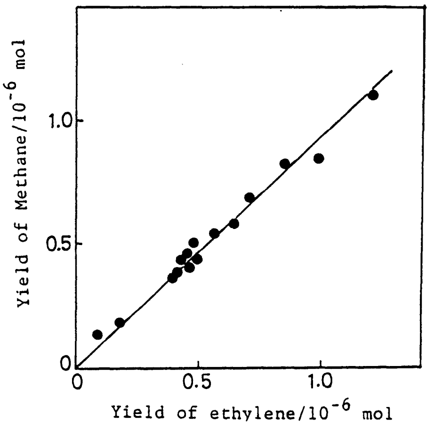

Fig. 5. Relation between yield of methane and that of ethylene.

photosensitized decomposition of propane at high temperatures,[1] and also to those of cadmium-photosensitized decomposition of propane obtained at the initial stage of reaction.[8] By following the mechanisms of $Hg(^3P_1)$-C_3H_8 and $Cd(^3P_1)$-C_3H_8 reactions, the zinc-photosensitized decomposition of propane could be discussed in terms of the following reactions:

$$Zn(^1S_0) + h\nu(307.6\text{ nm}) \rightarrow Zn(^3P_1) \tag{1}$$

$$Zn(^3P_1) \rightarrow Zn(^1S_0) + h\nu(307.6\text{ nm}) \tag{2}$$

$$Zn(^3P_1) + C_3H_8 \rightarrow ZnH + \alpha 1\text{-}C_3H_7 + (1-\alpha)2\text{-}C_3H_7 \tag{3}$$

$$ZnH \rightarrow Zn(^1S_0) + H \tag{4}$$

$$H + C_3H_8 \rightarrow H_2 + \beta 1\text{-}C_3H_7 + (1-\beta)2\text{-}C_3H_7 \tag{5}$$

$$1\text{-}C_3H_7 \rightarrow CH_3 + C_2H_4 \tag{6}$$

$$CH_3 + C_3H_8 \rightarrow CH_4 + \gamma 1\text{-}C_3H_7 + (1-\gamma)2\text{-}C_3H_7 \tag{7}$$

$$(H, CH_3, 1\text{-}C_3H_7, 2\text{-}C_3H_7) \rightarrow \text{recombination and disproportionation products} \tag{8}$$

Production of DMB and minor products is explained by Reactions (8).

From the above mechanism, the following relationships can be derived by neglecting Reactions (8):

$$\Phi_{H_2} = \frac{k_3[C_3H_8]}{k_2 + k_3[C_3H_8]} \tag{9}$$

and

$$\frac{\Phi_{CH_4}}{\Phi_{H_2}} = \frac{\Phi_{C_2H_4}}{\Phi_{H_2}} = (\alpha+\beta)(1+\gamma+\gamma^2+\cdots). \tag{10}$$

The quenching cross section of $Zn(^3P_J)$ by propane at 578 K was reported to be 6.94×10^{-16} cm^2.[9] This shows that k_2 in Eq. 9 can be neglected at all pressures examined here. This indicates that Φ_{H_2} is unity and is independent of the pressure. These findings are in agreement with observations during the initial stage of the reaction. As Fig. 3 shows, Φ_{H_2} is almost unity and is hardly dependent on the propane pressure at pressures higher than 20000 Pa. At lower pressures, however, Φ_{H_2} is considerably smaller than unity and depends on the propane pressure. This anomalous behavior at lower pressures and the nonlinear dependence of the hydrogen yield on time (espetially at lower pressures) shown in Fig. 2 seems to be due to the influence of the products. This point will be discussed later.

As Fig. 5 shows, the yield of ethylene is almost equal to that of methane under all conditions examined; this is in agreement with the prediction from Eq. 10. This shows that Reactions (8) can be neglected concerning the formation of methane and ethylene.

From the quenching cross sections of $Zn(^3P_J)$ by various hydrocarbons, the effective cross sections per primary C-H bond and secondary C-H bond were found to be 0.62×10^{-16} and 2.4×10^{-16} cm^2 at 578 K respectively.[9] As has been described previously,[10] the quenching rate of $Zn(^3P_1)$ by alkanes depends on the temperature. From the activation energies reported for the quenching of $Zn(^3P_1)$ by primary and secondary C-H bonds,[10] the cross sections per primary and secondary C-H bond at 633 K were estimated to be 1.1×10^{-16} and 3.9×10^{-16} cm^2, respectively. Using these values the value of α can be calculated as follows:

$$\frac{\alpha}{1-\alpha} = \frac{1.1\times6}{3.9\times2}, \text{ then } \alpha = 0.46.$$

Gunning et al.[12] gave a ratio of $\beta/(1-\beta)$ as 1.29 $\exp(-2000/1.987T)$, which is equal to 0.26 at 633 K. This value gives β=0.21. By assuming that γ is also equal to 0.21, we obtained $\Phi_{CH_4}/\Phi_{H_2}=\Phi_{C_2H_4}/\Phi_{H_2}=0.84$ from Eq. 10. This value is in fair agreement with the experimental values (0.72 for Φ_{CH_4}/Φ_{H_2} and 0.78 for $\Phi_{C_2H_4}/\Phi_{H_2}$). DMB is formed from a recombination of isopropyl radical and the steady-state concentration of this radical is probably proportional to the light intensity. This is in agreement with the tendency shown in Fig. 1.

Table 2 shows a comparison of the product formation in zinc-, cadmium-, and mercury-photosensitized decompositions of propane. The dependences of product formation on the time and propane pressure in the zinc-photosensitized decomposition of propane is different from those in the cadmium-photosensitized decomposition, but is similar to those in the mercury-photosensitized decomposition at high temperature. The dissimilarity of the cadmium-photosensitized decomposition to two other photosensitized decompositions can be ascribed to the large difference in the quenching cross section of propane and hydrogen in the case of cadmium ($\sigma_Q(H_2)/\sigma_Q(C_3H_8)$=6.2, 1500, and 3.7, for Zn,[9] Cd,[13] and Hg[14]). It was pointed out that the effect of hydrogen on the decomposition of propane must be important in the cadmium-photosensitized decomposition.[8]

We examined the effect on the product formation of the addition of *cis*-2-butene as a radical scavenger, of which the zinc-photosensitized reaction was studied in detail.[15] When *cis*-2-butene was added to propane, the quantum yields of hydrogen, methane, and ethylene

Table 2. Comparison of Product Formation in Zinc-, Cadmium-, and Mercury-Photosensitized Decomposition of Propane

Dependence on	R_{H_2}			R_{CH_4}/R_{H_2}			$R_{C_2H_4}/R_{H_2}$		
	Zn	Cd[a]	Hg[b]	Zn	Cd[a]	Hg[b]	Zn	Cd[a]	Hg[b]
Time	C(D[c])	I	C	C	D	C	C	D	—
Pressure	I(C[d])	I	I	C	C	—	C	—	—

C; constant, I; increase, D; decrease. a) At 265 °C, Ref. 8. b) At 300 °C, Ref. 1. c) At lower pressures. d) At shorter reaction times.

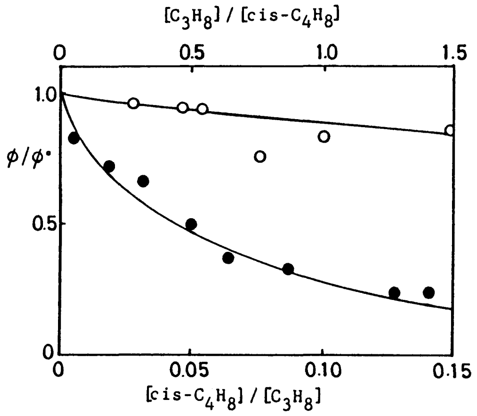

Fig. 6. Plots of $\Phi_{t\text{-}C_4H_8}/\Phi^\circ_{t\text{-}C_4H_8}$ against $[C_3H_8]/[cis\text{-}C_4H_8]$ (○), and of $\Phi_{H_2}/\Phi^\circ_{H_2}$ against $[cis\text{-}C_4H_8]/[C_3H_8]$ (●).

decreased as the quantum yield of *trans*-2-butene formation increased with an increase in the *cis*-2-butene pressure. Figure 6 shows the effect of *cis*-2-butene on the yield of hydrogen and the effect of propane on the yield of *trans*-2-butene. The following reactions are proposed to explain these effects:

$$\mathrm{Zn(^1S_0)} + h\nu(307.6\ \mathrm{nm}) \rightarrow \mathrm{Zn(^3P_1)} \tag{1}$$

$$\mathrm{Zn(^3P_1)} + \mathrm{C_3H_8} \rightarrow \mathrm{ZnH} + \alpha 1\text{-}\mathrm{C_3H_7} + (1-\alpha)2\text{-}\mathrm{C_3H_7} \tag{3}$$

$$\mathrm{ZnH} \rightarrow \mathrm{Zn(^1S_0)} + \mathrm{H} \tag{4}$$

$$\mathrm{Zn(^3P_1)} + cis\text{-}\mathrm{C_4H_8} \rightarrow \mathrm{Zn\text{-}C_4H_8^*} \tag{11}$$

$$\mathrm{H} + \mathrm{C_3H_8} \rightarrow \mathrm{H_2} + \beta 1\text{-}\mathrm{C_3H_7} + (1-\beta)2\text{-}\mathrm{C_3H_7} \tag{5}$$

$$\mathrm{H} + cis\text{-}\mathrm{C_4H_8} \rightarrow \mathrm{C_4H_9} \tag{12}$$

$$1\text{-}\mathrm{C_3H_7} \rightarrow \mathrm{CH_3} + \mathrm{C_2H_4} \tag{6}$$

$$\mathrm{CH_3} + \mathrm{C_3H_8} \rightarrow \mathrm{CH_4} + \gamma 1\text{-}\mathrm{C_3H_7} + (1-\gamma)2\text{-}\mathrm{C_3H_7} \tag{7}$$

$$\mathrm{Zn\text{-}C_4H_8^*} \rightarrow \mathrm{Zn(^1S_0)} + \delta trans\text{-}\mathrm{C_4H_8} + (1-\delta) cis\text{-}\mathrm{C_4H_8} \tag{13}$$

In the above, $\mathrm{Zn\text{-}C_4H_8^*}$ is a transient triplet addition complex formed between an excited zinc atom and a *cis*-2-butene molecule. The value of δ has been reported to be 0.6 at 633 K.[15] From the above reactions, the quantum yields of *trans*-2-butene and hydrogen can be expressed as follows:

$$\Phi_{t\text{-}C_4H_8} = \delta \frac{k_{11}[cis\text{-}C_4H_8]}{k_3[C_3H_8] + k_{11}[cis\text{-}C_4H_8]} \tag{14}$$

and

$$\Phi_{H_2} = \frac{k_3[C_3H_8]}{k_3[C_3H_8] + k_{11}[cis\text{-}C_4H_8]} \cdot \frac{k_5[C_3H_8]}{k_5[C_3H_8] + k_{12}[cis\text{-}C_4H_8]} \tag{15}$$

Therefore,

$$\frac{\Phi_{t\text{-}C_4H_8}}{\Phi^\circ_{t\text{-}C_4H_8}} = \frac{1}{1 + \dfrac{k_3[C_3H_8]}{k_{11}[cis\text{-}C_4H_8]}} \tag{16}$$

and

$$\frac{\Phi_{H_2}}{\Phi^\circ_{H_2}} = \frac{1}{1 + \dfrac{k_{11}[cis\text{-}C_4H_8]}{k_3[C_3H_8]}} \cdot \frac{1}{1 + \dfrac{k_{12}[cis\text{-}C_4H_8]}{k_5[C_3H_8]}} \tag{17}$$

Here, $\Phi^\circ_{t\text{-}C_4H_8}$ is the quantum yield of *trans*-2-butene in the absence of propane and $\Phi^\circ_{H_2}$ is the quantum yield of hydrogen in the absence of *cis*-2-butene.

As has been described previously,[10] the quenching rate of $\mathrm{Zn(^3P_J)}$ by alkane depends on the temperature. The values of k_3 and k_{11} at 578 K were reported to be 4.74×10^{-11}[9] and 8.58×10^{-10} ml molecule^{-1} s^{-1}.[15] From the activation energies for the quenching of $\mathrm{Zn(^3P_J)}$ by primary and secondary C-H bonds, the k_3-value at 633 K was estimated to be 1.0×10^{-10} ml molecule^{-1} s^{-1}. By assuming that k_{11} is not temperature dependent, the value of k_{11}/k_3 at 633 K can be obtained ($k_{11}/k_3=8.58$). The upper solid line in Fig. 6 shows the value of $\Phi_{t\text{-}C_4H_8}/\Phi^\circ_{t\text{-}C_4H_8}$ calculated by using the above value for k_{11}/k_3. The agreement between the observed and calculated values is fair.

The value of k_5 at 633 K has been estimated to be 2.86×10^{-10} ml molecule^{-1} s^{-1} from the equation $k_5=10^{14.16}\exp(-8350/1.987T)$ ml mol^{-1} s^{-1} reported by Baker et al.[16] Unfortunately, the value of k_{12} at 633 K has not been obtained. We estimated this value as follows: The rate constant at 633 K for the $\mathrm{H}+\mathrm{C_2H_4}\rightarrow\mathrm{C_2H_5}$ reaction has been estimated to be 3.65×10^{-12} ml molecule^{-1} s^{-1} from the equation $10^{12.9}\exp(-1500/1.987T)$ ml mol^{-1} s^{-1} obtained by Penzhonn and Darwent.[17] If we assume that the ratio of $k_{12}(c\text{-}C_4H_8)/k_{12}(C_2H_4)$ obtained at 298 K by Cvetanovic[18] is independent of temperature, we obtain $k_{12}/k_5=10.5$. By using this value, we calculated $\Phi_{H_2}/\Phi^\circ_{H_2}$ as a function of $[c\text{-}C_4H_8]/[C_3H_8]$. This is shown in Fig. 6 by a solid line. The calculated value of $\Phi_{H_2}/\Phi^\circ_{H_2}$ is in fair agreement with the observed one.

Figure 7 shows the pressure dependence of the quantum yield for hydrogen production obtained at irradiation time of 20 min, and Fig. 8 shows the time dependence of the quantum yield obtained at 1700 and 30000 Pa. As mentioned above, the influence of products on the hydrogen yield can not be neglected. Of the products formed, hydrogen and ethylene seem to have large effects because of their large amounts compared with those of other products, their large cross sections for quenching of excited zinc atoms, and their high reactivities to hydrogen atom produced in the initial stage of reaction. The following reactions are considered to explain the pressure and time dependences of the hydrogen yield:

$$\mathrm{Zn(^3P_1)} + \mathrm{C_3H_8} \rightarrow \mathrm{ZnH} + \alpha 1\text{-}\mathrm{C_3H_7} + (1-\alpha)2\text{-}\mathrm{C_3H_7} \tag{3}$$

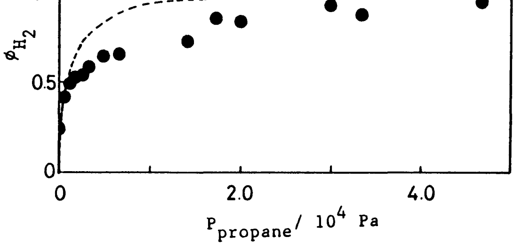

Fig. 7. Pressure dependence of quantum yield of hydrogen.

$$Zn(^3P_1)+H_2\rightarrow ZnH+H \qquad (18)$$

$$Zn(^3P_1)+C_2H_4\rightarrow Zn\text{-}C_2H_4{}^* \qquad (19)$$

$$ZnH\rightarrow Zn(^1S_0)+H \qquad (4)$$

$$H+C_3H_8\rightarrow H_2+\beta 1\text{-}C_3H_7+(1-\beta)2\text{-}C_3H_7 \qquad (5)$$

$$H+C_2H_4\rightarrow C_2H_5 \qquad (20)$$

From the above reactions, the rate of hydrogen production can be expressed as follows:

$$R_{H_2}=I_0\,\frac{k_3[C_3H_8]+2k_{18}[H_2]}{k_3[C_3H_8]+k_{18}[H_2]+k_{19}[C_2H_4]}\cdot\frac{k_5[C_3H_8]}{k_5[C_3H_8]+k_{20}[C_2H_4]} \qquad (21)$$

Here, we assume that hydrogen and ethylene are produced linearly with time and that their rates are independent of the initial propane pressure as a first approximation (at 20 min 1.8×10^{-6} mol of ethylene and 2.0×10^{-6} mol of hydrogen were obtained, therefore, at 633 K and in the 57 ml reaction cell at irradiation time of t min, $[C_2H_4]=6.3\times 10^{14}\,t$ molecule/ml and $[H_2]=7.0\times 10^{14}\,t$ molecule/ml). At 633 K and p Pa of propane $[C_3H_8]=1.14\times 10^{14}\,p$ molecule/ml. By using following rate constants,

$k_3 = 10.0\times 10^{-11}$ ml molecule^{-1} s^{-1},
$k_{18} = 106.6\times 10^{-11}$ ml molecule^{-1} s^{-1},
$k_{19} = 121.7\times 10^{-11}$ ml molecule^{-1} s^{-1},
$k_5 = 2.86\times 10^{-13}$ ml molecule^{-1} s^{-1},

and

$k_{20} = 3.65\times 10^{-12}$ ml molecule^{-1} s^{-1},

the rate for hydrogen formation can be rewritten as

$$R_{H_2}=I_0\,\frac{1.14p+14.9t}{1.14p+15.1t}\cdot\frac{3.26p}{3.26p+23.0t}\,. \qquad (22)$$

The value of $(1.14p+14.9t)/(1.14p+15.1t)$ is close to unity in the region of the pressure (67—40000 Pa) and time (0—40 min) examined here. Therefore, the quantum yield for hydrogen production can be expressed approximately by

$$\Phi_{H_2}=\frac{\int_0^t R_{H_2}\,dt}{I_0 t}=\frac{\int_0^t \frac{3.26p}{3.26p+230t}\,dt}{t}=\frac{3.26p}{t}\,\frac{1}{230}\ln\left(1+\frac{230t}{3.26p}\right)=\frac{0.0141p}{t}\ln\left(1+70.8\,\frac{t}{p}\right). \qquad (23)$$

In Figs. 7 and 8, the dashed lines indicate the pressure dependence and the time dependence of the quantum yield of hydrogen calculated according to the above equation. The agreement between the observed and the calculated values is not very good, but the decrease in the quantum yield with decreasing propane pressure and with increasing reaction time could be explained qualitatively by the above treatment regarding the influence of the products.

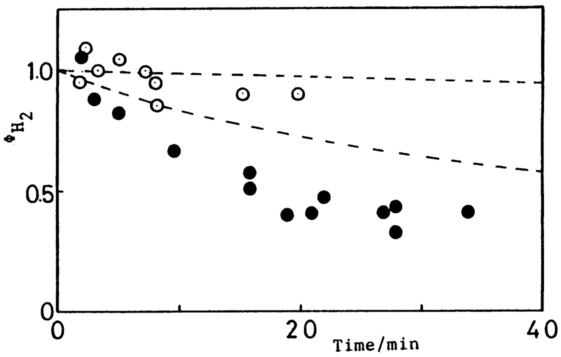

Fig. 8. Time dependence of quantum yield of hydrogen. ○: 30000 Pa, ●: 1700 Pa.

The quantum yield of hydrogen is somewhat smaller than the value predicted from the correlation mentioned above. In this manner, the decrease in the quantum yield of hydrogen must be mainly explained by the influence of ethylene on the production of hydrogen, but partly by other factors. The additional factors may include the influence of propylene and other products which react easily with hydrogen atom. We tried to identify these factors, were not successful. The origin of these factors remains an open question.

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