the observed phase behavior can be reproduced by using a simple model with reasonable values of the parameters in the model, despite the fact that neither the entropy of mixing for the surfactant nor the electrostatic forces are modeled in an unambiguous

Finally, the results in this work could have important practical implications. In a vast number of colloidal formulations, water-soluble polymers like EHEC and MC are present. They may be added to a system in order to, inter alia, improve the rheology and workability in water-based paint, act as an emulsifier in foods, or act as a protective colloid in cosmetic emulsions. In such a system it is very common that ionic surfactants and salt are also present and from the present investigation it is evident that this eventually could lead to unwanted effects. Thus, if a strong polymer-surfactant interaction occurs, this could result in, for example, a phase separation (clouding) and a loss in viscosity.

As we have seen, the interaction is strongly dependent on small amounts of salt, particularly if a relatively hydrophobic polymer like EHEC is used. Furthermore, the presence of salt may in some cases be unavoidable, whereas in other cases it proves to be time-consuming and costly to remove. However, according to our data this disadvantage could be overcome by the following measures: (1) either increase or decrease the surfactant concentration, (2) either lengthen or shorten the alkyl chain of the surfactant, or (3) if an anionic surfactant is used, change to a cationic one

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# Photocatalytic Reactions of 1,3-Butadiene over Water-Adsorbed TiO<sub>2</sub>

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Photocatalytic reactions of 1,3-butadiene over water-adsorbed TiO<sub>2</sub> were investigated at 293 K. The initial formation rates of  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_6$ ,  $C_3H_8$ ,  $1-C_4H_8$ , and trans-2- $C_4H_8$ , which hardly depend on the pressure of 1,3-butadiene (2.0–13.3 kPa), were 8.1, 7.1, 267, 177, 209, and 34 pmol s<sup>-1</sup>, respectively. The formations of CH<sub>4</sub>, n-C<sub>4</sub>H<sub>10</sub>, CO, n-C<sub>3</sub>H<sub>7</sub>CHO, s-C<sub>4</sub>H<sub>9</sub>OH, and n-C<sub>4</sub>H<sub>9</sub>OH were also observed. The drastic decrease of the hydrocarbon yields by the addition of O<sub>2</sub> was not found except for C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>. The increase of formation yield by the loading of Pt was observed for all products, especially n-C<sub>4</sub>H<sub>10</sub>. From these results, the reaction mechanisms that the photoformed OH radical and H atom at close range are concerned cooperatively were proposed for the formations of  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_6$ , and  $C_3H_8$  by the photocatalytic hydrogenolysis reaction. From the reaction mechanisms and the initial formation rates for the hydrogenolysis, it was found that the addition of OH to the C(1) position of 1,3-butadiene is 29.2 times faster than that to the C(2) position. No cis-2-butene was observed, though trans-2-butene and 1-butene resulting from the addition of two H atoms to 1,3-butadiene were found. It suggests that the geometrical structure of 1,3-butadiene (trans form) is conserved during the hydrogenation reaction. The photocatalytic hydrogenolysis and hydrogenation reaction rates are 1.9 and 5.4 times faster than those of cis-2-butene, respectively. These results are explainable by the facts that both addition rates of OH and H to 1,3-butadiene in the vapor phase are faster than those to cis-2-butene.

### Introduction

The photocatalytic reactions of alkenes and alkynes with water have been investigated with TiO<sub>2</sub>, 1-5 TiO<sub>2</sub> and TiO<sub>2</sub>-doped Fe<sub>2</sub>O<sub>3</sub>,6 TiO<sub>2</sub> anchored onto porous Vycor glass, <sup>7</sup> Ti-Si<sup>8</sup> and Ti-Al<sup>9</sup> binary oxides, metal-loaded TiO2,10 and CdS loaded with Pt or Rh.11 From these results, it was found that the major products are alkanes formed by hydrogenolysis reactions and that the hydrogenation reactions of alkenes and alkynes are markedly enhanced by loading of metals.4,5

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Recently, the yields of products formed by the photocatalytic reactions of cis-2-butene over water-adsorbed TiO<sub>2</sub> were observed as a function of the irradiation time and the incident light intensity.<sup>12</sup> It was found that the initial formation rates of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> formed by the hydrogenolysis reaction and n-C<sub>4</sub>H<sub>10</sub> produced by the hydrogenation reaction are proportional to the relative light intensity  $(I_r)$  and that the initial isomerization rates to trans-2-butene and 1-butene are proportional to  $I_r^{1/2}$ . From the results, the reaction mechanisms proceeding by the additions to cis-2-butene of the photoformed OH radical and H atom at close range for the hydrogenolysis, two H atoms for the hydrogenation, and OH radical for the isomerization were proposed. The same reaction behaviors were also found in the photocatalytic reactions of cis-2-pentene over water-adsorbed TiO<sub>2</sub>.13

Since 1,3-butadiene has a conjugated double bond, it arouses interest in the expectation that the photocatalytic reactions of 1,3-butadiene over water-adsorbed TiO<sub>2</sub> may be considerably different from those for allkenes such as cis-2-butene. Previously, it was reported that C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and trace CH<sub>4</sub> are formed by the photocatalytic reactions of 1,3-butadiene.<sup>2</sup> However, the details for the reaction mechanisms are not clear. Thus, the photocatalytic reactions of 1,3-butadiene over water-adsorbed TiO2 were in-

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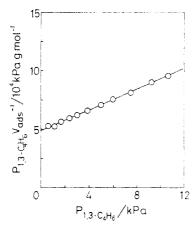
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<sup>(12)</sup> Kodama, S.; Yagi, S. J. Phys. Chem. 1989, 93, 4556.

<sup>(13)</sup> We have also investigated for the photocatalytic reactions of  $C_2H_2$ ,  $C_2H_4$ ,  $CH_3C \equiv CH$ ,  $C_3H_6$ , 1-butene, isobutene, trans-2-butene, and cis-2pentene over water-adsorbed TiO2.



**Figure 1.** Plot of  $P_{1,3\text{-C}_4\text{H}_6}V_{\text{ads}}^{-1}$  versus  $P_{1,3\text{-C}_4\text{H}_6}$  for the adsorption isotherm of 1,3-butadiene on water-adsorbed TiO<sub>2</sub> at 293 K.

vestigated in the present work to elucidate more detailed reaction mechanisms.

## **Experimental Section**

1,3-Butadiene obtained from Takachiho Kagakukogyo Co. was 99.6% pure. TiO<sub>2</sub> catalyst was prepared by drying at 373 K the precipitate formed by adding aqueous ammonia to an aqueous solution of TiCl<sub>4</sub>, calcinating at 773 K for 3 h in air, and reducing to powder with a mortar.<sup>14</sup>

A high-pressure mercury lamp of 100 W (Toshiba SHL-100UV) was used as a light source. The reaction cell was a quartz cylinder of 50-mm i.d. and 10-mm length. The volume of reaction system including the cell was 26.5 mL. Prior to the experiment, 500 mg of  $\text{TiO}_2$  catalyst that had been spread in the reaction cell was heated at 773 K for 1 h in the presence of  $\text{O}_2$  and was well evacuated at the same temperature.

The adsorption of water on  $TiO_2$  was performed by introducing about 2 kPa of water vapor and evacuating at room temperature after 10 min. The photocatalytic reaction was carried out by introducing 2.0–13.3 kPa of 1,3-butadiene on the water-adsorbed  $TiO_2$  and by irradiating UV light into the cell immersed in a water bath maintained at 293 K.

Gas samples were taken at definite intervals and analyzed by gas chromatography with a dimethylsulfolane column (6 m) at 292 K, a silica gel column (2 m) at 353 K, and a poly(ethylene glycol) 400 column (2 m) at 333 K.

### Results

The prepared  $TiO_2$  catalyst was found to have the anatase structure from the X-ray diffraction. The surface area of  $TiO_2$  catalyst was determined to be 36.4 m² g⁻¹ from the BET method by supposing that the area of  $N_2$  molecule as an adsorbate is 16.2 Ų.¹⁵ The irreversible adsorption amount of water vapor on  $TiO_2$  was 4.25 molecules nm⁻² at 293 K.

The adsorption amount of 1,3-butadiene on the water-adsorbed  $TiO_2$  ( $V_{ads}$ ) was measured as a function of the pressure of 1,3-butadiene at 293 K. On the basis of the Langmuir equation

$$\frac{P}{V_{\text{ads}}} = \frac{k_1/k_2}{V_{\text{max}}} + \frac{P}{V_{\text{max}}} \tag{1}$$

for the adsorption isotherm, <sup>16</sup> the relation of  $P_{1,3\text{-}C_4H_6}/V_{ads}$  versus  $P_{1,3\text{-}C_4H_6}$  was plotted in Figure 1, where  $k_1/k_2$  and  $V_{max}$  mean the rate constant ratio of desorption to adsorption and the maximum adsorption amount. From the intercept and the slope, the values of  $k_1/k_2 = 11.2$  kPa and  $V_{max} = 3.77$  molecules nm<sup>-2</sup> were obtained. In this case, no irreversible adsorption was found.

TABLE I: Formation Amounts of the Products after 60 min on the Photocatalytic Reaction of 1,3-Butadiene (4.0 kPa) over Water-Adsorbed TiO,

	formation amount, nmol			
product	$\overline{\text{TiO}_2}^a$	$O_2/TiO_2^b$	Pt/TiO2	
CH <sub>4</sub>	13	14	27	
C <sub>2</sub> H <sub>4</sub>	25	81	36	
$C_2H_6$	22	1	50	
$C_1H_6$	507	760	836	
$C_3H_8$	613	2	1096	
1-C <sub>4</sub> H <sub>8</sub>	385	39	619	
trans-2-C <sub>4</sub> H <sub>8</sub>	86	21	236	
n-C <sub>4</sub> H <sub>10</sub>	9	3	127	

 $^aTiO_2$  without  $O_2.$   $^bTiO_2$  with  $O_2$  (1.7 kPa).  $^cTiO_2$  loaded with Pt (4 wt %).

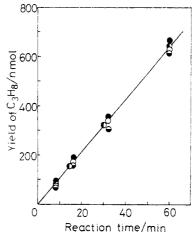


Figure 2. Formation yield of  $C_3H_8$  measured as functions of the pressure of 1,3-butadiene and the irradiation time on the photocatalytic reaction over water-adsorbed TiO<sub>2</sub>: pressure of 1,3-butadiene ( $\bullet$ ) 2.0 kPa; ( $\bullet$ ) 4.0 kPa; ( $\circ$ ) 13.3 kPa.

The hydrocarbon products formed by the photocatalytic reactions of 1,3-butadiene over water-adsorbed TiO<sub>2</sub> were CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, 1-butene, *trans*-2-butene, and *n*-C<sub>4</sub>H<sub>10</sub>. These products were also found in the photocatalytic reactions on water-adsorbed TiO<sub>2</sub> with O<sub>2</sub> of 1.7 kPa (O<sub>2</sub>/TiO<sub>2</sub>) and on water-adsorbed TiO<sub>2</sub> loaded with 4 wt % Pt black without the O<sub>2</sub> pretreatment at 773 K (Pt/TiO<sub>2</sub>). The amounts of products formed by UV irradiation for 60 min at 4.0 kPa of 1,3-butadiene and 293 K are shown in Table I.

For the oxygen-containing products, the formation of CO that is equivalent to the formation amount of  $C_3H_8$  was found by the combustion method with a CuO column at 620 K. The trace formations of n- $C_3H_7$ CHO, s- $C_4H_9$ OH, and n- $C_4H_9$ OH were also found by gas chromatographic analysis with a poly(ethylene glycol) column. Meanwhile, the polymerization of 1,3-butadiene seems to proceed from the result that the amount of 1,3-butadiene as a reactant decreases markedly with UV irradiation. The formation of  $H_2$  was not found.

The formation yields of  $C_3H_8$ , 1- $C_4H_8$ , and n- $C_4H_{10}$  that were measured as functions of the pressure of 1,3-butadiene and the UV irradiation time are shown in Figures 2-4. It is found in Figures 2 and 3 that the formation yields of  $C_3H_8$  and 1- $C_4H_8$  are not proportional to the pressure of 1,3-butadiene and that the initial formation rates are much the same regardless of the pressure of 1,3-butadiene. The same trends were also found for  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_6$ , and trans-2-butene. The initial formation rates of these products were estimated by using appropriate empirical functions for the formation yield and the reaction time<sup>12</sup> and are shown in Table II.

Meanwhile, it is found in Figure 4 that the formation yield of  $n\text{-}\mathrm{C}_4H_{10}$  increases rapidly with an increase of the irradiation time, but the initial formation rate is actually zero. The same trend was also found for CH<sub>4</sub>. These results suggest that CH<sub>4</sub> and  $n\text{-}\mathrm{C}_4H_{10}$  are not formed as a primary product.

<sup>(14)</sup> Itoh, M.; Hattori, H.; Tanabe, K. J. Catal. 1974, 35, 225. Hattori, H.; Itoh, M.; Tanabe, K. Ibid. 1975, 38, 172. Itoh, M.; Hattori, H.; Tanabe, K. Ibid. 1976, 43, 192.

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 (16) Barrow, G. M. Physical Chemistry; McGraw-Hill: New York, 1961;
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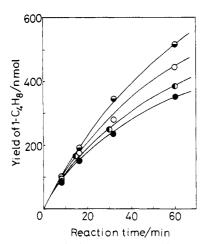


Figure 3. Formation yield of 1-butene observed as functions of the pressure of 1,3-butadiene and the irradiation time on the photocatalytic reaction over water-adsorbed TiO<sub>2</sub>: pressure of 1,3-butadiene (●) 2.0 kPa; (●) 4.0 kPa; (●) 8.0 kPa; (●) 13.3 kPa.

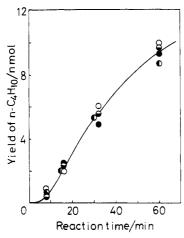


Figure 4. Formation yield of n-C<sub>4</sub>H<sub>10</sub> measured as functions of the pressure of 1,3-butadiene and the reaction time on the photocatalytic reaction over water-adsorbed TiO<sub>2</sub>: pressure of 1,3-butadiene ( $\bullet$ ) 2.0 kPa; ( $\bullet$ ) 4.0 kPa; ( $\circ$ ) 8.0 kPa; ( $\circ$ ) 13.3 kPa.

TABLE II: Initial Formation Rate of the Products Formed by the Photocatalytic Reaction of 1,3-Butadiene over Water-Adsorbed TiO<sub>2</sub> and Enthalpy Change of the Reactions in Schemes I-V

product	R°, pmol s <sup>-1</sup>	ΔH° <sub>298</sub> , kJ mol <sup>-1</sup>
C <sub>2</sub> H <sub>4</sub>	8.1	-480.9
C <sub>2</sub> H <sub>6</sub>	7.1	-512.4
$C_3H_6$	267	-462.5
$C_3H_8$	177	-581.5
1-C <sub>4</sub> H <sub>8</sub>	209	-546.3
trans-2-C <sub>4</sub> H <sub>8</sub>	34	-557.3

With azomethane as an actinometer, it was found that the incident light intensity into the reaction cell is about  $1.5 \times 10^{17}$  quanta s<sup>-1</sup> for UV light below 410 nm. The result means that the initial formation rate of 1 pmol s<sup>-1</sup> corresponds to the quantum yield of about  $4 \times 10^{-6}$ .

#### Discussion

Reaction Mechanisms. By irradiation of UV light to TiO<sub>2</sub>, which is a semiconductor, the electron (e<sup>-</sup>) in the conduction band and the positive hole (h<sup>+</sup>) in the valence band are formed:

$$(TiO_2) + h\nu \rightarrow h^+ + e^-$$
 (2)

When H<sup>+</sup> and OH<sup>-</sup> ions exist on the surfaces of TiO<sub>2</sub>, H atoms and OH radicals are formed because the photoformed electrons and holes are trapped into these ions:<sup>4,17</sup>

$$e^- + H^+ \to H \tag{3}$$

$$h^+ + OH^- \rightarrow OH$$
 (4)

SCHEME III

$$CH_{2}CHCH = CH_{2} \longrightarrow CH_{2} - -CH_{2}CH = CH_{2}$$

$$CH_{2} - -CH_{2}CH = CH_{3}$$

$$CH_{2} - -CH_{2} - -CH_{3}$$

$$CH_{2} - -CH_{3}$$

$$CH_{2} - -CH_{3}$$

$$CH_{2} - -CH_{3}$$

$$CH_{2} - -CH_{3}$$

$$CH_{3} - -CH_{3}$$

$$CH_{4} - -CH_{3}$$

$$CH_{4} - -CH_{3}$$

$$CH_{4} - -CH_{3}$$

$$CH_{5} - -CH_{5}$$

$$CH_{6} - -CH_{3}$$

$$CH_{7} - -CH_{7}$$

$$CH_{7}$$

In previous work,  $^{12}$  the reaction mechanisms proceeding by additions to the  $\pi$  bonds of the OH radical and H atom at close range were proposed for the formations of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> by the photocatalytic hydrogenolysis of *cis*-2-butene. In light of the mechanisms and the experimental results obtained on the photocatalytic hydrogenolyses of various hydrocarbons over wateradsorbed TiO<sub>2</sub>,  $^{13}$  the reaction mechanisms for the formations of C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub> by the hydrogenolysis of 1,3-butadiene were postulated as Schemes I–IV.

Scheme II (the radical intermediate mechanism) is supported by the fact that the formation of  $C_2H_6$  decreases drastically with the addition of  $O_2$ . Scheme IV, including the radical intermediate, is supported by the following facts: the formation yield of  $C_3H_8$  decreases drastically in the presence of  $O_2$ ; trace formation of n- $C_3H_7$ CHO is found; CO of nearly the same amount as  $C_3H_8$  is formed.

The initial formation rate of CH<sub>4</sub> is zero, though the yield increases quickly with an increase of the irradiation time, similarly as the trend for n-C<sub>4</sub>H<sub>10</sub> in Figure 4. Therefore, the formation of CH<sub>4</sub> seems to arise from subsequent hydrogenolyses of CH<sub>3</sub>CHO(ads), CH<sub>2</sub>=C=O(ads), C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, and butenes formed by the photocatalytic reactions of 1,3-butadiene. <sup>12,13</sup>

In the light of the mechanism for the photocatalytic hydrogenations of C<sub>2</sub>H<sub>4</sub><sup>11</sup> and *cis*-2-butene, <sup>12</sup> Scheme V was postulated

<sup>(17)</sup> Herrmann, J. M.; Disdier, J.; Mozzanega, M.-N.; Pichat, P. J. Catal. 1979, 60, 369. Sato, S.; White, J. M. Ibid. 1981, 69, 128. Ohno, M.; Uzawa, H.; Miyazaki, T.; Tarama, K. Chem. Lett. 1987, 779. Hussein, F. H.; Rudham, R. J. Chem. Soc., Faraday Trans. I 1987, 83, 1631. Ohtani, B.; Kakimoto, M.; Miyadzu, H.; Nishimoto, S.; Kagiya, T. J. Phys. Chem. 1988, 92, 5773.

SCHEME V

$$CH_{2}CHCH = CH_{2} \longrightarrow 1-butene$$

$$\downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow$$

$$CH_{2} = CHCH = CH_{2} + 2\dot{H}$$

$$CH_{2}CH = CHCH_{2} \longrightarrow trans-2-butene$$

$$\downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow$$

$$\downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow$$

$$\downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow$$

$$\downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow \qquad \downarrow$$

for the formations of 1-butene and *trans*-2-butene. The formation of n-C<sub>4</sub>H<sub>10</sub> appears to result from further hydrogenations of 1-butene and *trans*-2-butene formed by Scheme V, because the initial formation rate of n-C<sub>4</sub>H<sub>10</sub> is zero as is seen in Figure 4.

For the trace formations of oxygen-containing products, n- $C_3H_7CHO$  seems to result from the stabilization of the intermediate  $O=CHCH_2CH_2CH_3$  (Scheme IV) formed by the addition reaction of OH radical and H atom to 1,3-butadiene, which is very exothermic. The formations of n- $C_4H_9OH$  and s- $C_4H_9OH$  may be caused by further hydrogenation of radicals formed by the additions of OH to the C(1) and C(2) positions of 1,3-butadiene, respectively. The finding of these products supports the mechanisms that the photocatalytic hydrogenolysis reactions proceed via the additions of OH radical and H atom.

The extreme decrease on the formation yields of hydrocarbon products by the addition of  $O_2$  was not found except for  $C_2H_6$  and  $C_3H_8$  as is seen in Table I. The result may be because the direct quenching by  $O_2$  of the photoformed H atoms and OH radicals is protected by 1,3-butadiene adsorbed upon water-adsorbed  $TiO_2$ . Meanwhile, the formation yields of  $C_2H_6$  and  $C_3H_8$  decrease drastically by the addition of  $O_2$ . The result suggests that the radical intermediates in Schemes II and IV are directly quenched by  $O_2$ . On the other hand, the increase of  $C_2H_4$  and  $C_3H_6$  yields by the addition of  $O_2$  may be caused by the reactions of  $O_2$  with radical intermediates formed by additions of H atom and OH radical of 1,3-butadiene.

The formation yields of  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_6$ , and  $C_3H_8$  by the hydrogenolysis reactions increase by loading Pt black on  $TiO_2$  catalyst as is seen in Table I. It may be because the recombination reactions between the photoformed electrons and positive holes are suppressed as the results that the photoformed ellectrons are gathered into Pt and both carriers are separated. It is known that the photocatalytic hydrogenation is markedly enhanced by loading of Pt.<sup>4,5</sup> In fact, the yields of 1-butene and trans-2-butene increase by loading of Pt. Moreover, the yield of n- $C_4H_{10}$  increases drastically with Pt. The result suggests that butenes formed by the photocatalytic hydrogenation of 1,3-butadiene are further hydrogenized on Pt to form n- $C_4H_{10}$ .

On the photocatalytic hydrogenation, the formation of cis-2-butene was not found. The fact suggests that the hydrogenations of 1,3-butadiene (trans form) to 1-butene (trans form) and trans-2-butene proceed effectively and that the hydrogenation to cis-2-butene accompanying the internal rotation about the C-(2)-C(3) axis does not proceed due to the strengthening of the C(2)-C(3) bond by the additions of two H atoms to the C(1) and C(4) positions of 1,3-butadiene, that is, the geometrical structure of trans form is conserved during the hydrogenation reaction.

The double-bond shift isomerization of 1,3-butadiene to 1,2-butadiene can be expected to proceed by the same reaction mechanism as the photocatalytic isomerizations of *cis*-2-butene to 1-butene and of CH=CCH<sub>3</sub> to CH<sub>2</sub>=C=CH<sub>2</sub> over wateradsorbed TiO<sub>2</sub>:<sup>12</sup>

However, the isomerization was hardly observed, though the double bond shift isomerizations from cis-2-butene ( $R^{\circ} = 2230$ 

TABLE III: Comparisons of  $k_{OH}$ ,  $k_{H}$ ,  $\sum R_{d}^{\circ}$ , and  $\sum R_{h}^{\circ}$ 

rate constant	1,3-butadiene	cis-2-butene	
$k_{\rm OH}, 10^{-12} {\rm cm}^3 {\rm molecule}^{-1} {\rm s}^{-1}$	67.84	54.7b	_
$k_{\rm H}$ , $10^{-12}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$8.5^c$	1.05 <sup>d</sup>	
$k_{\rm OH}/k_{\rm H}$	8.0	52	
$\sum R^{\circ}_{d}$ , pmol s <sup>-1</sup>	459	245°	
$\sum R^{\circ}_{h}$ , pmol s <sup>-1</sup>	243	45°	

<sup>a</sup> Reference 21. <sup>b</sup> Reference 26. <sup>c</sup> Reference 22. <sup>d</sup> Reference 27. <sup>e</sup> Reference 12.

pmol s<sup>-1</sup>)<sup>12</sup> and CH=CCH<sub>3</sub> ( $R^{\circ}$  = 251 pmol s<sup>-1</sup>)<sup>13</sup> proceed effectively. This may be because the efficiency of the addition of OH radical to the C(2) position of 1,3-butadiene is much less than that to the C(1) position as is discussed later and because the isomerization from 1,3-butadiene is highly endothermic ( $\Delta H^{\circ}_{298}$  = 52.1 kJ mol<sup>-1</sup>) as compared with those from cis-2-butene ( $\Delta H^{\circ}_{298}$  = 6.7 kJ mol<sup>-1</sup>) and CH=CCH<sub>3</sub> ( $\Delta H^{\circ}_{298}$  = 6.9 kJ mol<sup>-1</sup>). <sup>18</sup>

The enthalpy changes of the reactions in Schemes I-V were estimated by using the standard heats of formation in the vapor phase at 1 atm and 298 K,<sup>18</sup> because the enthalpies in the adsorption state are unknown. It was found that all of the reactions are very exothermic with enthalpy changes lower than -460 kJ mol<sup>-1</sup> as is seen in Table II and are energetically possible.

Comparisons of Reaction Rates. The average surface area per one  $TiO_2$  molecule of anatase type titania (S) was estimated to be 10.6 Å<sup>2</sup> from the reaction

$$S = [M/(\rho N_{\rm A})]^{2/3} \tag{5}$$

Here, M,  $\rho$ , and  $N_{\rm A}$  mean the molecular weight of TiO<sub>2</sub> (79.90), the density of anatase type TiO<sub>2</sub> (3.84 g cm<sup>-3</sup>), and Avogadro's number. Meanwhile, the ratio of the number of irreversibly adsorbed water molecules to the number of Ti<sup>4+</sup> ions on the catalyst surface was estimated to be 0.451 from the surface area of the catalyst (36.4 m<sup>2</sup> g<sup>-1</sup>), the irreversible adsorption amount of water (4.25 molecules nm<sup>-2</sup>), and the average surface area per TiO<sub>2</sub> molecule (10.6 Å<sup>2</sup>). The result suggests that one OH<sup>-</sup> ion per Ti<sup>4+</sup> ion exists on the catalyst surface, when it is assumed that water molecules are adsorbed dissociatively<sup>19</sup> and that the number of OH<sup>-</sup> ions remaining on surface of the catalyst calcinated at 773 K is 0.098 of the number of Ti<sup>4+</sup> ions on the catalyst surface.<sup>20</sup>

From the value of  $V_{\rm max}=3.77$  molecules nm<sup>-2</sup> for the reversible adsorption of 1,3-butadiene on water-adsorbed TiO<sub>2</sub>, it was found that the surface of water-adsorbed TiO<sub>2</sub> is covered by a monolayer of 1,3-butadiene at the limiting high pressure and 293 K, when the molecular cross section of 1,3-butadiene is assumed to be 26.5 Å<sup>2</sup>. The assumption seems to be reasonable judging from the molecular cross sections of CH<sub>4</sub> (18.1 Å<sup>2</sup>) and n-C<sub>4</sub>H<sub>10</sub> (32.1 Å<sup>2</sup>).<sup>15</sup> The surface coverage by 1,3-butadiene ( $\theta_b$ ) is calculable from the relation of  $\theta_b = V_{\rm ads}/V_{\rm max}$  and the value of  $k_1/k_2 = 11.2$  kPa in eq 1. Then, it was found to be  $\theta_b = 0.15$ -0.54 in the pressure range 2.0-13.3 kPa of 1,3-butadiene.

On the other hand, the initial formation rates of the hydrocabon products hardly depend on the pressure of 1,3-butadiene. This suggests that the additions of OH radical and H atom to 1,3-butadiene in Schemes I-V are not the rate-determining step for the following reasons: the catalyst surface is covered by 1,3-butadiene with high coverage; 1,3-butadiene molecules concerning in the reaction are fully supplied from the vapor phase because the number of 1,3-butadiene molecules striking the catalyst surface per unit time is about 10<sup>12</sup> times larger than the number of 1,3-butadiene molecules consumed by the photocatalytic reaction.

Since the specific addition rate of OH radical to 1,3-butadiene in the vapor phase at 298 K ( $k_{\rm OH}$ ) is 8.0 times higher than that

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TABLE IV: Frontier Electron Densities and Charge Distribution on Each Position of the CH<sub>2</sub>---CH---CH<sub>3</sub> Radical

	-		•		
position	$f_r^{(E)}$	$f_r^{(N)}$	$f_r^{(R)}$	$q_{\rm r}$	
C(1)	0.798	0.689	0.975	-0.110	
C(2)	0.533	0.477	0.040	-0.066	
C(3)	0.581	0.774	0.897	0.100	
C(4)	0.089	0.060	0.088	0.076	

for H atom  $(k_{\rm H})$  as is seen in Table III,  $^{21,22}$  the addition of OH to 1,3-butadiene seems to proceed in advance of the addition of H. On the other hand, it is found in Schemes I-IV that C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> result from the addition of OH to the C(2) position of 1,3-butadiene and that C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> are derived from the addition of OH to the C(1) position. Then, the rate ratio

$$(R^{\circ}_{C_1H_6} + R^{\circ}_{C_1H_8})/(R^{\circ}_{C_2H_4} + R^{\circ}_{C_2H_6}) = 29.2$$

is obtained. The ratio means that the addition efficiency of OH to the C(1) position of 1,3-butadiene is 29 times higher than that to the C(2) position. Similar results were also found on the photocatalytic hydrogenolyses of CH<sub>2</sub>=CHCH<sub>3</sub>, CH<sub>2</sub>=C(CH<sub>3</sub>)<sub>2</sub>, and CH≡CCH<sub>3</sub> over water-adsorbed TiO<sub>2</sub>. 13

It is in general known that the position having a high free valence index is more reactive than the position having a low index for the reactions with free radicals.<sup>23</sup> From the Hückel approximation, the free valence indexes of the C(1) and C(2)positions of 1,3-butadiene were estimated to be 0.839 and 0.390, respectively. Thus, the experimental fact that the C(1) position is very reactive for the reaction with OH radical is supported by the quantum chemical consideration.

For the photocatalytic hydrogenation of 1,3-butadiene, the position of the first addition of H atom can be expected to be C(1), similar to the case of the addition of OH radical. Therefore, the divergence where 1-butene or 2-butene is formed depends on the position of the second addition of H atom.

According to the frontier electron theory,<sup>24</sup> the reactive position in a radical for the electrophilic, nucleophilic, and radical attack reactions can be estimated from the frontier electron densities:

$$f_r^{(E)} = (c_r^{\text{ho}})^2 + (c_r^{\text{so}})^2$$
 (6)

$$f_r^{(N)} = (c_r^{so})^2 + (c_r^{lu})^2$$
 (7)

$$f_r^{(R)} = 2(c_r^{so})^2$$
 (8)

Here,  $f_r^{(E)}$ ,  $f_r^{(N)}$ , and  $f_r^{(R)}$  mean the electron densities for the electrophilic, nucleophilic, and radical attack reactions, respectively.  $c_r^{ho}$ ,  $c_r^{so}$ ,  $c_r^{lu}$  denote the coefficients of rth position of the highest occupied, singly occupied, and lowest unoccupied molecular orbitals, respectively.

The frontier electron densities of the radical formed by the addition of H atom to the terminal carbon of 1,3-butadiene were calculated by using the Hückel approximation with due regard to the hyperconjugation with CH<sub>3</sub> group:<sup>25</sup>

Here,  $\alpha$  and  $\beta$  mean the Coulomb and resonance integrals. The results are shown in Table IV together with the values of the charge distribution  $(q_r)$ . Since  $f_1^{(R)}$  is higher than  $f_3^{(R)}$ , the formation yield of 2-butene can be expected to be higher than the yield of 1-butene, whereas the experimental yield of 1-butene is 6.1 times higher than the yield of 2-butene. This finding suggests that the reaction behavior of the radical on the catalyst surface is different from that in the vapor phase by the interactions with surface sites.

From the values of  $f_r^{(E)}$  and  $f_r^{(N)}$  or  $q_r$ , it is found that the C(1) and C(3) positions of the radical are effective for the electrophilic and nucleophilic reactions, respectively. Therefore, it is imaginable that C(1) and C(3) interact with Ti<sup>4+</sup> (or H<sup>+</sup>) and O<sup>2-</sup> (or OH<sup>-</sup>) on the catalyst surface, respectively:

However, the interaction of C(1) and Ti<sup>4+</sup> is conceivably more effective than that of C(3) with O<sup>2-</sup>, judging from the values of  $f_r^{(E)}$ ,  $f_r^{(N)}$ , and  $q_r$  and the numbers of charges of Ti<sup>4+</sup> and O<sup>2-</sup> ions. Thus, the low formation yield of 2-butene may be because the addition of H atom to C(1) is disturbed by the blocking of C(1) by the Ti<sup>4+</sup> ion.

The total formation rate of the hydrocarbon products by the photocatalytic hydrogenolysis of 1,3-butadiene is 1.9 times faster than that of cis-2-butene:12

$$\frac{[R^{\circ}_{C_{2}H_{4}} + R^{\circ}_{C_{2}H_{6}} + R^{\circ}_{C_{3}H_{6}} + R^{\circ}_{C_{3}H_{8}}]_{1,3\text{-butadiene}}}{[R^{\circ}_{C_{1}H_{4}} + R^{\circ}_{C_{3}H_{6}}]_{cis\text{-}2\text{-butene}}} = 1.9$$

The result is supported by the fact that both  $k_{\rm OH}$  and  $k_{\rm H}$  for 1,3-butadiene are larger than those of cis-2-butene<sup>26,27</sup> as is seen in Table III. The total formation rate of the products by the photocatalytic hydrogenation of 1,3-butadiene is 5.4 times faster than that for cis-2-butene:12

$$\frac{[R^{\circ}_{1-C_{4}H_{8}} + R^{\circ}_{trans-2-C_{4}H_{8}}]_{1,3-butadiene}}{[R^{\circ}_{n-C_{4}H_{10}}]_{cis-2-butene}} = 5.4$$

The result is also explainable by the fact that  $k_H$  for 1,3-butadiene is much larger than  $k_H$  for cis-2-butene.

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