Photocatalytic Hydrogenation, Decomposition and Isomerization Reactions of Alkenes over TiO₂-adsorbed Water

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Photocatalytic reactions of alkenes over TiO₂-adsorbed water have been investigated. The products are hydrogenated molecules (C_nH_{2n+2}) formed by the addition of two H atoms to the π bond of the alkene $(C_nH_{2n}, 2 \le n \le 4)$ and lower alkanes $(CH_4, C_{n-2}H_{2n-2} \text{ and } C_{n-1}H_{2n})$ formed by the cooperative addition of an H atom and an OH radical to the π bond followed by decomposition. The photocatalytic isomerization of butenes by surface OH radicals is also observed. The generalized reaction mechanisms for these photocatalytic reactions have been postulated. The initial rate of formation of the hydrogenation product and the sum of the initial rates of formation of lower alkanes per amount of alkene adsorbed are proportional to $k_{\rm H}$ and $(k_{\rm H}k_{\rm OH})^{1/2}$, respectively. Here, $k_{\rm H}$ and $k_{\rm OH}$ are rate constants for addition of H atoms and OH radicals to alkene in the vapour phase. For photocatalytic isomerizations, it is found that the isomerization of (E)-but-2-ene to but-1-ene (*trans* form) which has the same geometrical form is about twice as effective as that between (Z)-but-2-ene and but-1-ene and that the addition of OH to the C(1) position of but-1-ene prevents the isomerization to but-2-enes.

For photocatalytic reactions of alkenes over TiO_2 -adsorbed water,¹⁻⁶ it was found that the major products are alkanes having a lower carbon number than the alkene, and that the hydrogenation of alkenes is markedly enhanced by loading of metals.^{5,6} It was also found that the photocatalytic isomerization between butenes over TiO_2 proceeds with high yield.⁷⁻⁹

Recently, the yields of products formed by the photocatalytic reactions of (Z)-but-2-ene over TiO_2 -adsorbed water were observed as functions of the irradiation time and the incident light intensity.¹⁰ The initial rates of formation of CH₄ and C₂H₆ as decomposition products and *n*-C₄H₁₀ as a hydrogenation product are proportional to the light intensity and the initial isomerization rates to (*E*)-2-C₄H₈ and 1-C₄H₈ are proportional to the square root of the light intensity.

The mechanisms for these reactions were proposed from the notion that important roles are played by the photoformed OH radical and H atom at close range, for the formation of lower alkanes, by a pair of H atoms, for the hydrogenation, and by OH radical, for the isomerizations. The mechanisms of the photocatalytic reactions of buta-1,3diene over TiO₂-adsorbed water can also be explained on the basis of the same notion.¹¹

The photocatalytic reactions of various alkenes over TiO_2 -adsorbed water were investigated in this work to examine the intrinsic nature of the photocatalytic hydrogenation, decomposition and isomerization reactions from correlations between the properties of the reactants and the initial rates of formation of products.

Experimental

Ethene, propene, isobutene, but-1-ene and (*E*)-but-2-ene were obtained from Takachiho Kagakukogyo Co. and their purities were >99.2%. TiO₂ catalyst was prepared by drying, at 373 K, the precipitate formed by addition of aqueous ammonia to an aqueous solution of TiCl₄, calcining at 773 K for 3 h in air and reducing to powder with a mortar.¹²

The reaction cell was a quartz cylinder of 50 mm inner diameter and 10 mm length. The volume of the reaction system including the cell was 26.5 cm^3 . Prior to the experiment, 500 mg of TiO₂ catalyst which had been spread in the

reaction cell were heated at 773 K for 1 h in the presence of O_2 and evacuated at the same temperature. The irreversible adsorption of water on TiO₂ was performed by introducing *ca.* 2 kPa of water vapour and evacuating at room temperature.

The photocatalytic reaction was carried out by introducing 4.0 kPa of alkene to TiO_2 -adsorbed water and by irradiating with UV light (mainly 366 nm) from a high-pressure 100 W mercury lamp (Toshiba, SHL-100UV), with the reaction cell maintained at 293 K. Gas samples were taken at intervals and analysed by gas chromatography with a dimethyl-sulfolane column (6 m) at 292 K and a silica gel column (2 m) at 353 K. The oxygen-containing products were analysed using a poly(ethylene glycol) 400 column (4 m) at 343 K.

Results

The surface area of the TiO₂ catalyst, which has the anatase structure, was 36.4 m² g^{-1.11} The amount of irreversibly adsorbed water vapour on TiO₂ at 293 K was 257 μ mol g⁻¹, which corresponds to one half of the total Ti⁴⁺ ions on the surface.^{10,11} The amount of alkene reversibly adsorbed by 0.5 g of TiO₂-adsorbed water (V_{ads}) was measured as a function of the pressure of alkene (P) at 293 K. The results are shown in Fig. 1.

The hydrocarbon products formed by the photocatalytic reactions of but-1-ene over TiO₂-adsorbed water were CH₄, C_2H_6 , C_3H_8 , n- C_4H_{10} , (E)-2- C_4H_8 and (Z)-2- C_4H_8 . The yields of these products, measured as a function of the irradiation time, are shown in Fig. 2. The yields of CH₄, C_2H_6 , C_3H_8 , n- C_4H_{10} , 1- C_4H_8 and (Z)-2- C_4H_8 formed by the photocatalytic reactions of (E)-but-2-ene are shown in Fig. 3 as a function of the irradiation time. Similarly, CH₄ and C_2H_6 from ethene, CH₄, C_2H_6 and C_3H_8 from propene and CH₄, C_3H_8 and *i*- C_4H_{10} from isobutene were formed with the same irradiation-time dependences as those in Fig. 2.

By using empirical equations such as $Y = R^0 t/(1 + bt^m)$ (m < 1) and $Y = R^0 t/(1 + ct)^m (n \ge 1)$, the initial formation rates of products (R^0) were estimated from the intercept of the plots of t/Y vs. t^m or $(t/Y)^{1/n}$ vs. t. Here, Y and t are the yield and the reaction time, while, b and c denote constants that vary little with t. The initial formation rates obtained by such procedures are shown in Table 1 within an error of





Fig. 1 Pressure dependences of the amount of alkene reversibly adsorbed on TiO₂-adsorbed water (0.5 g) at 293 K. \oplus , But-1-ene; \bigcirc , (Z)-but-2-ene; \oplus , (E)-but-2-ene; \oplus , isobutene; \oplus , propene; \bigoplus , ethene

10%. An initial formation rate of 1 pmol s⁻¹ corresponds to a quantum yield of $ca. 4 \times 10^{-6.11}$

On the other hand, the initial formation rate of C_3H_8 from (*E*)-but-2-ene was found to be zero, as was the case for the formation of C_3H_8 from (*Z*)-but-2-ene.¹⁰ On the photo-catalytic reactions of propene over TiO₂-adsorbed water, formation of traces of H₂, CH₃COCH₃, *n*-C₃H₇OH and *i*-C₃H₇OH was observed. Meanwhile, no products from alkenes on TiO₂-adsorbed water were observed under dark conditions.



Fig. 2 Yields of products measured as a function of the irradiation time for the photocatalytic reaction of but-1-ene over TiO_2 -adsorbed water. \bullet , Propane; \bullet , (*E*)-but-2-ene; \bigcirc , (*Z*)-but-2-ene; \bullet , ethene; \bullet , *n*-butane; \bullet , methane (\times 5)



Fig. 3 Irradiation-time dependences of the yields of the photocatalytic reaction of (E)-but-2-ene over TiO₂-adsorbed water. \bigoplus , But-1-ene; \bigcirc , (Z)-but-2-ene; \bigoplus , ethane (× 5); \bigoplus , *n*-butane (× 20); \bigoplus , methane (× 30); \bigoplus , propane (× 30)

Strong UV absorption by the TiO₂ catalyst was found in the short-wavelength range ($\lambda < 400$ nm) and the emission spectrum from the mercury lamp was particularly intense at 366 nm. Thus, the most effective wavelength for the photocatalytic reaction was found to be 366 nm.

Discussion

Adsorption State of Alkenes

The Langmuir equation for the adsorption isotherm is given by eqn. (1).¹³

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

Here, V_{max} and k_1/k_2 are the maximum amount of adsorption and the rate constant ratio of desorption to adsorption. The values of k_1/k_2 and V_{max} obtained from the intercept and the slope of the plot of P/V_{ads} vs. P by using the data in Fig. 1 are shown in Table 2 together with the amount of adsorption at 4.0 kPa, $V_{\text{ads}}(4.0)$.

From the density of liquid (ρ) , the molecular weight (M) and Avogadro's number (N_A) , the average diameter of a molecule (d) may be calculated approximately from the equation.

$$d = (6M/\pi N_{\rm A} \rho)^{1/3} \tag{2}$$

The coverage occupied by the adsorbed molecules at 4.0 kPa $[\theta(4.0)]$ can then be calculated using the equation

$$\theta(4.0) = V_{ads}(4.0) N_A \pi d^2 / 4Sw$$
(3)

where S and w are surface area and the weight of the catalyst. The values of d and $\theta(4.0)$ calculated from eqn. (2) and (3) are also shown in Table 2. From these results, the coverage at 4.0 kPa was found to be in the range 0.05-0.30.

Reaction Mechanisms

On irradiation of TiO_2 , which is a semiconductor, with UV light, positive holes (h⁺) in the valence band and electrons

Table 1 Initial formation rates of products arising from the photocatalytic reactions of alkenes over TiO_2 -adsorbed water

	initial formation rate/pmol s ⁻¹						
reactant	CH ₄	C ₂ H ₆	C ₃ H ₈	<i>n</i> -C ₄ H ₁₀	$1-C_4H_8$	(E)-2-C ₄ H ₈	(Z)-2-C ₄ H ₈
C ₂ H ₄	30.5	13.7	······································				
C ₁ H ₆	6.5	193	8.9				
i-Č₄H ₈	12.8	0	444	178°	0	0	0
1-C₄H ₈	2.0	36.6	246	26.7		132	62
(Z) -2- $\check{C}_{4}H_{8}$	12.2	256	0 ^b	50.8	4470		2260
$(E)-2-C_4H_8^{a}$	8.7	236	0 ^b	45.0	2230	2450	

" Ref. 10. " The initial formation rate is zero, though formation by subsequent reactions is observed." The product is isobutane.

 (e^{-}) in the conduction band are formed.

$$(TiO_2) + hv \rightarrow h^+ + e^- \qquad (4)$$

When OH^- and H^+ ions are formed on the surface of TiO_2 by the adsorption of water, OH radicals and H atoms may be formed as a result of the trapping of the photoformed holes and electrons by these ions.^{5,14}

$$h^+ + OH^- \rightarrow \dot{O}H$$
 (5)

$$e^- + H^+ \to \dot{H}$$
 (6)

On the basis of the notion that the formation of lower alkanes (CH₄, $C_{n-2}H_{2n-2}$ and $C_{n-1}H_{2n}$) in the photocatalytic reaction of alkenes (C_nH_{2n}) over TiO₂-adsorbed water is caused by the cooperative addition to the π bond of an OH radical and an H atom at close range, and the decomposition of the addition intermediates in chemically activated states,^{10,11} Scheme 1 was postulated as a generalized reaction mechanism for the formation of lower alkanes.

$$C_{n}H_{2n} + \dot{O}H + \dot{H} \xrightarrow{(i)} R^{1} - C \xrightarrow{I} C - R^{4}$$

$$O - H \overset{I}{H}$$

$$\overset{(ii)}{\longrightarrow} R^{1} - C \xrightarrow{I} C + R^{4} \xrightarrow{(iii)} R^{1}R^{2}C = O \text{ (ads)} + R^{3}CH_{2}R^{4}$$

$$I$$

Scheme 1 Generalized mechanism for the formation of lower alkanes

The reaction sequences are as follows: (i) cooperative addition of an OH radical and an H atom to the π bond of the alkene; (ii) weakening of the C-C bond with concomitant strengthening of the C-O bond; (iii) decomposition of the intermediate I to give R¹R²C=O(ads) and R³CH₂R⁴. The formation of only traces of *n*-C₃H₇OH and *i*-C₃H₇OH from propene supports the reaction mechanism of Scheme 1, in which the majority of chemically activated alcohol formed by process (i) decomposes by processes (ii) and (iii). The photocatalytic reactions of Scheme 1 can also be written as follows:

$$C_{n}H_{2n} + \dot{O}H + \dot{H} \rightarrow HCHO(ads) + C_{n-1}H_{2n} \qquad (series A)$$

$$C_{n}H_{2n} + \dot{O}H + \dot{H} \rightarrow CH_{3}CHO(ads) + C_{n-2}H_{2n-2} \qquad (series B)$$

$$C_{n}H_{2n} + \dot{O}H + \dot{H} \rightarrow CH_{3}CHO(ads) + CH_{3}H_{2n-2} \qquad (series CH_{3}H_{2n-2})$$

 $C_nH_{2n} + OH + H \rightarrow C_2H_5CHO(ads) + CH_4$ (series C)

The hydrocarbon products $(\mathbb{R}^3 \mathbb{CH}_2 \mathbb{R}^4)$ identified and their initial formation rates (\mathbb{R}^0_d) are shown in Table 3 together with the functional groups $\mathbb{R}^1 - \mathbb{R}^4$.

The trace formation of propane from (E)-but-2-ene appears to result from the further reaction of but-1-ene, formed by the photocatalytic isomerization of (E)-but-2-ene, because the direct formation of propane from (E)-but-2-ene is not possible, similar to the case of (Z)-but-2-ene,¹⁰ though its formation from but-1-ene is possible according to the mechanism of Scheme 1. In addition, the formation of traces of H_2 and CH_3COCH_3 from propene suggests that the dehydrogenation of the chemically activated alcohol formed by process (i) occurs to some extent.

Table 3 Functional groups in the intermediate I and the initial formation rate (R_d^0) of alkanes $(R^3CH_2R^4)$ occurring by the mechanism of Scheme 1

	functional group				·	P 0	
reactant	R ¹	R ²	R ³	R⁴	R ³ CH ₂ R ⁴	R_d° /pmol s ⁻¹	
series A							
C ₂ H ₄	Н	н	Н	Н	CH₄	30.5	
C ₁ H ₆	Н	Н	н	CH ₁	$C_{2}H_{6}$	193	
1-C₄H ₈	Н	Н	Н	C,H,	C ₁ H ₈	246	
i-C ₄ H ₈	Н	Н	CH ₃	ĊH ₃	C_3H_8	444	
series B							
C ₃ H ₆	CH ₃	Н	Н	Н	CH₄	6.5	
1-Č₄H ₈	CH,	Н	Н	CH ₃	$C_{2}H_{6}$	36.6	
(Z) - $\tilde{2}$ - $\check{C}_{4}H_{8}$	CH,	Н	Н	CH,	C ₂ H ₆	236	
$(E)-2-C_4H_8$	CH ₃	Н	Н	CH ₃	$C_2H_6^{\circ}$	256	
series C							
1-C₄H.	C ₂ H ₄	Н	Н	Н	CH₄	2.0	
(Z)-2-C ₄ H ₂	C,H,	Н	н	Н	CH₄	8.7	
$(E)-2-C_4H_8$	C,H,	Н	Н	Н	CH₄	12.2	
i-C ₄ H ₈	ĊН ₃	CH ₃	Н	Н	CH ⁺ ₄	12.8	

 Table 2
 Data for the reversible adsorption of alkenes on TiO₂-adsorbed water at 293 K

adsorbate	(k ₁ /k ₂) /kPa	$V_{\max} / \mu mol g^{-1}$	$V_{ads}(4.0) / \mu mol g^{-1}$	d /nm	θ(4.0)
C ₃ H ₄	15.39	74.0	15.3	0.522	0.054
C ₁ H ₆	7.24	114.2	40.6	0.591	0.184
i-Č₄H ₈	7.09	120.2	43.3	0.642	0.232
1-C, H,	6.17	139.4	54.9	0.643	0.295
(<i>E</i>)-2-C ₄ H	5.74	116.4	47.8	0.665	0.275
$(Z)-2-C_4H_8$	6.96	139.2	50.8	0.659	0.287

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For the formation of ethane from ethene, propane from propene, *n*-butane from but-1-ene and but-2-enes and isobutane from isobutene, Scheme 2 was proposed on the basis of the reaction mechanisms for the photocatalytic hydrogenation of ethene,⁶ (Z)-but-2-ene¹⁰ and buta-1,3-diene.¹¹

$$C_nH_{2n} + 2\dot{H} \rightarrow C_nH_{2n+2}$$

Scheme 2 Mechanism of hydrogenation of alkenes

The photocatalytic hydrogenation seems to proceed by the addition of a pair of H atoms to the π bond of the alkene (C_nH_{2n}) to form alkane (C_nH_{2n+2}) .

The reaction mechanisms for the photocatalytic isomerization of (Z)-but-2-ene to (E)-but-2-ene and but-1-ene over TiO₂-adsorbed water have been proposed previously from the notion that the photoformed OH radical plays a significant role in the isomerizations.¹⁰ By applying the same notion to the photocatalytic isomerization of (E)-but-2-ene and but-1-ene, a collective reaction mechanism (Scheme 3) was postulated for the photocatalytic isomerizations of (Z)or (E)-but-2-ene to (E)- or (Z)-but-2-ene by the route (a)-(b)-(e)-(f), but-2-enes to but-1-ene by the route (a)-(b)-(d)-(g) and but-1-ene to but-2-enes by the route (c)-(d)-(e)-(f).

The reaction sequences for the isomerization of but-1-ene to but-2-enes by the route (c)-(d)-(e)-(f) are as follows: (c) addition of OH radical to the C(2) position of but-1-ene; (d) hydrogen abstraction from OH by $\dot{C}(1)$ and internal rotation about the C(2)-C(3) axis; (e) hydrogen abstraction from CH₂(3) by \dot{O} ; (f) formation of (E)- or (Z)-but-2-ene by the addition of an electron. Addition of the OH radical to the C(1) position of but-1-ene does not lead to but-2-enes owing to blocking of the C(1) position by OH by \dot{O}^{15}

$$CH_2 = CH - CH_2 - CH_3 \xrightarrow[e^-]{} CH_2 - CH_2 - CH_3$$

OH⁻ O-H
$$\xrightarrow{CH_2 - CH_2 - CH_2 - CH_3$$

OH⁻ O-H
O-H

The photocatalytic isomerization of (*E*)-but-2-ene to (*Z*)but-2-ene and but-1-ene over TiO_2 -adsorbed water seems to proceed ω , the same mechanism as that for (*Z*)-but-2-ene.¹⁰ The mechanisms in Scheme 3 are characterized in that all of the isomerizations proceed via the common intermediate II.

Reaction Kinetics

The sum of the initial formation rates of lower alkanes produced by Scheme 1, $\sum R_d^0$, can be expressed as

$$\sum R_d^0 = k_d[H][OH][C_n H_{2n}]_{ads}$$
(7)

provided that the rate-determining step is the addition process of the H atom and OH radical to the alkene. Here, [H] and [OH] denote the concentrations of H atoms and OH radicals on the catalyst surface, $[C_nH_{2n}]_{ads}$ means the concentration of alkene adsorbed on TiO₂-adsorbed water and $[C_nH_{2n}]_{ads}$ at 4.0 kPa is proportional to $V_{ads}(4.0)$, *i.e.* $[C_nH_{2n}]_{ads} = aV_{ads}(4.0)$.

Since the reaction in Scheme 1 proceeds by the cooperative addition of an H atom and an OH radical, the apparent rate constant (k_d) was assumed to be proportional to the geometric average of k_H and k_{OH} as an empirical equation including factors of both k_H and k_{OH} .

$$k_{\rm d} = \alpha (k_{\rm H} k_{\rm OH})^{1/2} \tag{8}$$

Here, $k_{\rm H}$ and $k_{\rm OH}$ are the rate constants for addition of H atoms and OH radicals respectively, to alkene in the vapour phase at 298 K. From these relations, eqn. (9) can be derived:

$$\sum R_{\rm d}^{\rm 0}/V_{\rm ads}(4.0) = a\alpha [{\rm H}] [{\rm OH}] (k_{\rm H} k_{\rm OH})^{1/2}$$
(9)

Since *a*, α , [H] and [OH] are constant in the early stages of the reaction, the relationship between $\sum R_d^0/V_{ads}(4.0)$ and $(k_{H}k_{OH})^{1/2}$ was plotted in Fig. 4 using the values of k_{H}^{16-19} and k_{OH}^{20-22} listed in Table 4. The linear relationship strongly suggests that the rate-determining step for the formation of lower alkanes is the cooperative addition of an H atom and an OH radical to the alkene.

The initial rate of formation of alkane from the hydrogenation reaction (R_h^0) can be expressed by eqn. (10), derived from Scheme 2.

$$R_{\rm h}^0 = k_{\rm h} [{\rm H}]^2 [{\rm C}_n {\rm H}_{2n}]_{\rm ads}$$
(10)



Fig. 4 $\sum_{n} R_{d}^{0}/V_{ads}(4.0)$ vs. $(k_{H}k_{OH})^{1/2}$. \bullet , Ethene; \bullet , propene; \bullet , (Z)-but-2-ene; \bigcirc , but-1-ene; \bullet , (E)-but-2-ene; \bigcirc , isobutene

$$CH_{3}-CH=CH-CH_{3}+OH^{-} \underbrace{(f)}_{e^{-}}CH_{3}-CH-CH-CH_{3}$$

$$CH_{3}-CH=CH-CH_{3} \xrightarrow{(a)} CH_{3}-CH-CH-CH_{3} \xrightarrow{(b)} O-H$$

$$O-H \xrightarrow{(b)} CH_{3}-CH+CH_{2}-CH_{3} \xrightarrow{(b)} CH_{3}-CH+CH_{2}-CH_{3} \xrightarrow{(b)} CH_{3}-CH+CH_{2}-CH_{3} \xrightarrow{(c)} CH_{3}-CH+CH_{2}-CH_{3} \xrightarrow{(c)} O-H$$

$$CH_{2}=CH-CH_{2}-CH_{3} \xrightarrow{(c)} CH_{2}-CH-CH_{2}-CH_{3} \xrightarrow{(c)} CH_{2}-CH_{3}+OH^{-} \xrightarrow{(c)} CH_{2}-CH-CH_{2}-CH_{3}+OH^{-}$$

Scheme 3 Photocatalytic isomerization mechanisms of butenes

 Table 4
 Rate constants for addition of OH radicals and H atoms to alkenes in the vapour phase at 298 K

reactant	$k_{\rm OH}/10^{-12} {\rm cm}^3$ molecule ⁻¹ s ⁻¹	$k_{\rm H}/10^{-12} {\rm cm}^3$ molecule ⁻¹ s ⁻¹	k _{oh} /k _h
C.H.	8.34ª	1.19 ^e	7.0
C ₁ H ₂	25.1 ^b	1.98 ^f	12.7
i-C₄H。	54.7°	4.87 ^g	11.2
1-C₄H _s	31.3°	2.00 ^g	15.7
(E)-2-C ₄ H ₂	65.1 ^d	1.159	56.5
$(Z)-2-C_{A}H_{8}$	57.1 ^d	1.05%	54.4

^a Ref. 16, ^b Ref. 17, ^c Ref. 18, ^d Ref. 19, ^e Ref. 20, ^f Ref. 21, ^g Ref. 22.

Since the reaction proceeds by the cooperative addition of two H atoms to the alkene, it was also assumed that the apparent rate constant (k_h) is proportional to the geometric average

$$k_{\rm h} = \beta (k_{\rm H} k_{\rm H})^{1/2} = \beta k_{\rm H} \tag{11}$$

From these relationships, eqn. (12) can be derived.

$$R_{\rm b}^0/V_{\rm ads}(4.0) = a\beta[{\rm H}]^2 k_{\rm H}$$
(12)

Since a, β and [H] are constant in the initial stage of the reaction, the relationship between $R_h^0/V_{ads}(4.0)$ and k_H was plotted in Fig. 5. The linear relationship suggests that the hydrogenation reaction of Scheme 2 proceeds by the co-operative addition of a pair of H atoms to the alkene.



Fig. 5 Relationship between $R_h^0/V_{ads}(4.0)$ and $k_H \cdot \oplus$, (Z)-But-2-ene; \bigoplus , ethene; \bigoplus , (E)-but-2-ene; \bigoplus , isobutene; \bigcirc , but-1-ene; \bigoplus , propene

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However, the reason for R_h^0/V_{ads} (4.0) for propene and but-1ene being fairly low is not clear for the present.

From the comparisons of eqn. (9) and (12) and the slopes in Fig. 4 and 5, the relation

$$\beta[\mathrm{H}]/\alpha[\mathrm{OH}] = 1.30 \tag{13}$$

can be derived. This result suggests that the hydrogenation reaction on the catalyst surface is more effective than that leading to lower alkanes.

From the reaction mechanism in Scheme 1, the product of series A is formed when OH radical is added to the C(1) position of $CH_2=CH-CH_3$, $CH_2=CH-C_2H_5$ and $CH_2=C(CH_3)_2$. Alternatively, the products of series B and C are formed when OH radical is added to the C(2) position. Therefore, it is possible to compare the initial rate of formation of products from addition of OH to the C(1) position $[R_d^0(1)]$ with the rate for addition to the C(2) position $[R_d^0(1)]$. These products and the values of $R_d^0(1)$, $R_d^0(2)$ and $R_d^0(1)/R_d^0(2)$ are shown in Table 5.

Table 5 shows that the values of $R_d^0(1)/R_d^0(2)$ are high, except for but-1-ene. This may be due to the fact that k_{OH} is much larger than k_H , as is seen in Table 4, and that the reactivity of the C(1) position towards radical attack is higher than that of the C(2) position because of the hyperconjugation between the π -bond system and the methyl group in propene and isobutene.^{11,23} However, $R_d^0(1)/R_d^0(2)$ for but-1ene is not so high and this may be because the hyperconjugation between the π -bond system and the ethyl group is weaker.

From the values in Table 1, the initial isomerization rates between butenes can be expressed in pmol s^{-1} as follows:

(Z)-but-2-ene
$$\frac{2450}{2260}$$
 (E)-but-2-ene
2230 62 132 4470
but-1-ene

It is found that the initial rate of isomerization of (E)-but-2ene to but-1-ene is twice as fast as the rate from (Z)-but-2-ene to but-1-ene. The same trend is also found for the isomerizations of but-1-ene to (E)- and (Z)-but-2-enes. This suggests that the isomerization between similar geometrical forms is more effective than isomerization between different forms.

On the other hand, all of the photocatalytic isomerizations between butenes proceed by passing through the intermediate II in Scheme 3. Therefore, the following simplified scheme was used for the reaction kinetics:

(Z)-but-2-ene
$$\frac{k_{Z-II}}{k_{H-Z}}$$
 CH₃-CH \leftrightarrow CH₂-CH₃ $\frac{k_{H-E_{\star}}}{k_{E-H}}$ (E)-but-2-ene
+ \dot{O} II + \dot{O} H k_{H-I}
 \dot{O} H k_{H-I} \dot{O} H \dot{O} H \dot{O} H

From the simplified scheme, the initial rates of isomerization from (Z)-but-2-ene to but-1-ene and (E)-but-2-ene,

Table 5 Products classified by the addition position of OH, their initial formation rates and the rate ratio

	product by addition position		D 0(1)	B ⁰ (2)		
reactant	C(1)	C(2)	$K_{a}^{(1)}$ /pmol s ⁻¹	$k_{d}(2)$ /pmol s ⁻¹	$R_{\rm d}^{\rm 0}(1)/R_{\rm d}^{\rm 0}(2)$	
$CH_2 = CH - CH_3$ $CH_2 = C(CH_3)_2$ $CH_2 = CH - C_2H_5$ $CH_2 = CH - CH = CH_2 $ ^a	$C_{2}H_{6}$ $C_{3}H_{8}$ $C_{3}H_{8}$ $C_{3}H_{6} + C_{3}H_{8}$	$CH_4 \\ CH_4 \\ CH_4 + C_2H_6 \\ C_2H_4 + C_2H_6$	193 444 246 444	6.5 12.8 38.6 15.2	29.7 34.7 6.4 29.2	

^a Ref. 11.

 $R_{Z \to 1}^0$ and $R_{Z \to E}^0$, are given by eqn. (14) and (15).

$$R_{Z \to 1}^{0} = \frac{k_{\Pi \to 1}}{k_{\Pi \to Z} + k_{\Pi \to E} + k_{\Pi \to 1}} \times k_{Z \to \Pi} [OH][(Z)-2-C_4H_8]_{ads}$$
(14)

$$R_{Z \to E}^{0} = \frac{k_{\Pi \to E}}{k_{\Pi \to Z} + k_{\Pi \to E} + k_{\Pi \to 1}}$$
$$\times k_{Z \to \Pi} [OH] [(Z) - 2 - C_4 H_8]_{ads}$$
(15)

By combining both equations, eqn. (16) is obtained.

1.

$$k_{\rm II \to 1} / k_{\rm II \to E} = R^{\rm 0}_{\rm Z \to 1} / R^{\rm 0}_{\rm Z \to E}$$
(16)

Using the same procedure, eqn. (17) and (18) may be derived.

$$k_{\rm II \to 1} / k_{\rm II \to Z} = R^{\rm 0}_{\rm E \to 1} / R^{\rm 0}_{\rm E \to Z}$$
(17)

$$k_{\mathrm{II} \to \mathrm{E}}/k_{\mathrm{II} \to \mathrm{Z}} = R_{1 \to \mathrm{E}}^{0}/R_{1 \to \mathrm{Z}}^{0}$$
(18)

By applying the values in Table 1 to eqn. (16)–(18), the values of $k_{\Pi \to I}/k_{\Pi \to E} = 0.910$, $k_{\Pi \to 1}/k_{\Pi \to Z} = 1.98$ and $k_{\Pi \to E}/k_{\Pi \to Z} = 2.13$ were obtained. Meanwhile, the value of $k_{\Pi \to E}/k_{\Pi \to Z} = 2.17$ was obtained from the equation

$$k_{\rm II \to E}/k_{\rm II \to Z} = (R^0_{\rm Z \to E}/R^0_{\rm Z \to 1})(R^0_{\rm Z \to 1}/R^0_{\rm E \to Z})$$
(19)

derived by combining eqn. (16) and (17) and is in accord with the value obtained from eqn. (18). The consistency suggests that the treatment by the simplified scheme is adequate. Then, the average value of 2.15 was adopted for $k_{\Pi \to E}/k_{\Pi \to Z}$.

For $R_{Z \to 1}^0$ and $R_{1 \to E}^0$, eqn. (20) and (21) can be derived.

$$R_{E\to1}^{0} = \frac{k_{\Pi\to1}}{k_{\Pi\to2} + k_{\Pi\toE} + k_{\Pi\to1}} \times k_{E\to\Pi} [OH][(E)-2-C_4H_8]_{ads}$$
(20)

$$R_{1 \to E}^{0} = \frac{k_{\Pi \to E}}{k_{\Pi \to Z} + k_{\Pi \to E} + k_{\Pi \to 1}}$$
$$\times k_{1 \to \Pi} [OH] [1 - C_4 H_8]_{ads}$$
(21)

Then, eqn. (22) and (23) can be derived from eqn. (14), (15), (20) and (21).

$$\frac{k_{\rm E \to II}}{k_{\rm Z \to II}} = \frac{R_{\rm E \to 1}^0}{R_{\rm Z \to 1}^0} \frac{[(Z)-2-C_4H_8]_{\rm ads}}{[(E)-2-C_4H_8]_{\rm ads}}$$
(22)

$$\frac{k_{1 \to \Pi}}{k_{2 \to \Pi}} = \frac{R_{1 \to E}^{0}}{R_{2 \to E}^{0}} \frac{[(Z) - 2 - C_{4}H_{8}]_{ads}}{[1 - C_{4}H_{8}]_{ads}}$$
(23)

The concentration ratio is given by the ratio of $V_{ads}(4.0)$ of butenes. From the values in Tables 1 and 2, the values $k_{\rm E \to II}/k_{\rm Z \to II} = 2.13$ and $k_{1 \to II}/k_{\rm Z \to II} = 0.050$ were obtained.

From these rate constant ratios, the rate constants, relative to $k_{Z \to II}$ and $k_{II \to Z}$ can be expressed as follows:

(Z)-but-2-ene
$$\frac{1.00}{1.00}$$
 intermediate II $\frac{2.13}{2.15}$ (E)-but-2-ene
 $0.050 \Big| 1.98$
but-1-ene

The transitions between (E)-but-2-ene and the intermediate II and the reaction from the intermediate II to but-1-ene (*trans* form) are about twice as fast as those between (Z)-but-

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2-ene and II. These results suggest that the *E* form of II, which is thermodynamically stable, is more abundant than the *Z* form of II, and that the hydrogen abstraction efficiency by \dot{O} from CH₃(1) group in II is nearly equal to the efficiency of abstraction from the CH₂(3) group.

On the other hand, the reaction from but-1-ene to II is extremely slow compared with the others. This may be because the addition of OH radical to the reactive C(1) position of but-1-ene does not lead to the intermediate II as discussed above. Meanwhile, the photocatalytic isomerizations arising from H atom replacing the OH radical seem to be slight, because $k_{\rm H}/k_{\rm OH}$ values for butenes are very small.

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