the two-dimensional bimolecular rate constant to be in the region of 10^{11} dm² mol⁻¹ s⁻¹. This quantity is almost 3 orders of magnitude smaller than that for silica.

Conclusions

1. On silica the main adsorbate is hydrogen-bonded acridine. The TTA of this species is readily detected at 435 nm, and the decay is first-order ($\tau = 30$ ms) for samples of low coverage or when the oxide substrate is pretreated at $T_a > 500$ °C. For other conditions the decay is faster and nonexponential. Delayed fluorescence from the hydrogen-bonded species is observed in samples of high coverage or low T_a .

2. On alumina the acridinium cation, AH^+ , is the main adsorbate for low T_a , while σ -bonded acridine is mainly present at high T_a . Strong triplet-triplet absorption at 480 nm is seen for AH^+ , and the decay is nonexponential. Weak transient absorption is recorded for samples of high T_a , and no delayed fluorescence is observed under any of the experimental conditions employed here. 3. Mobility of adsorbed acridine accounts for the bimolecular processes seen on silica when pretreated at low T_a . Under this condition Si-OH groups predominate on the surface and translational motion of the adsorbate has a small activation barrier. At high T_a Si-OH groups are largely replaced by Si-O-Si units which present a higher barrier to lateral mobility, and under this condition virtually no bimolecular phenomena occur.

4. Mobility on the surface of alumina is very restricted. At low T_a AH⁺ is trapped at -OH groups, and at high T_a the adsorbates are trapped at Lewis-acid centers; all the trapping sites have high activation barriers to translational motion. Therefore, no bimolecular processes are detected on this adsorbent.

Acknowledgment. This work was performed under EEC Contract No. STI-016-J-C and also supported by the Deutsche Forschungsgemeinschaft (Oe 57/12-2), and U.S. Army (DAJA 45-85-C-0010).

Registry No. Al₂O₃, 1344-28-1; SiO₂, 7631-86-9; acridine, 260-94-6; acridinium, 22559-71-3.

Reaction Mechanisms for the Photocatalytic Isomerization and Hydrogenation of cis-2-Butene over TiO₂

Sukeya Kodama* and Shinji Yagi

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan (Received: August 2, 1988; In Final Form: December 9, 1988)

Photocatalytic isomerization and hydrogenation of *cis*-2-butene over TiO₂ and water-adsorbed TiO₂ were investigated. The reaction products were 1-butene and *trans*-2-butene on TiO₂ and were CH₄, C₂H₆, C₃H₈, *n*-C₄H₁₀, 1-butene, and *trans*-2-butene on water-adsorbed TiO₂. The formation amounts of these products were observed as functions of the reaction time and the light intensity. The initial rates (R^0) in 10⁻⁹ mol s⁻¹ units, measured as a function of the relative light intensity (I_r), were $R^0(1-C_4H_8) = 6.09I_r + 1.21I_r^{1/2}$ and $R^0(trans-2-C_4H_8) = 3.39I_r + 3.35I_r^{1/2}$ on TiO₂ and $R^0(CH_4) = 0.0087I_r$, $R^0(C_2H_6) = 0.236I_r$, $R^0(n-C_4H_{10}) = 0.045I_r$, $R^0(1-C_4H_8) = 2.23I_r^{1/2}$, and $R^0(trans-2-C_4H_8) = 2.45I_r^{1/2}$ on water-adsorbed TiO₂. No C_3H_8 as a primary product was found. From these results, it was found that the reaction modes of four kinds exist on the photocatalytic isomerization of *cis*-2-butene over TiO₂ and the overall isomerization rate on TiO₂ is about 50 times faster as compared with the total hydrogenation rate to CH₄, C_2H_6 , and $n-C_4H_{10}$ on water-adsorbed TiO₂ at $I_r = 1$. Reaction to 1-butene depending on I_r ; Ti³⁺, O⁻, and OH⁻ for the isomerizations to 1-butene and *trans*-2-butene depending on $I_r^{1/2}$; OH and H for the hydrogenolyses to CH₄ and C₂H₆; and 2H for the hydrogenation to *n*-C₄H₁₀ are concerned in their formations were postulated.

Introduction

The photocatalytic isomerizations of butenes have been investigated previously with TiO_2 ,^{1,2} ZnO,^{1,3} SnO₂,³ CdS,⁴ and ZnS,^{4,5} and Ti-Si⁶ and Ti-Al⁷ binary metal oxides. It was found from these results that both cis-trans and double bond shift isomerizations for 2-butenes proceed over TiO_2 and ZnO, only cis-trans isomerization of 2-butenes takes place over SnO_2 , CdS, and ZnS, and the isomerization of 1-butene to 2-butenes proceeds hardly over the metal oxides and sulfides. It was also suggested that the photoformed O⁻ and $Ti^{3+}(Zn^+)$ –O⁻ pairs play significant roles on the photocatalytic isomerizations over the metal oxides.^{1-3,6} Moreover, a reaction mechanism that $Ti^{3+}(Zn^+)$, O⁻, and surface

 \mathbf{OH}^- are concerned cooperatively in the isomerization to 1-butene of 2-butenes was postulated.^3

Morikawa et al.⁸ have studied the photocatalytic isomerization of *n*-butenes on porous Vycor glass and suggested that the cis-trans isomerization proceeds via a cationic intermediate of 2-butene formed on a site of Lewis acid character. On the photocatalytic cis-trans isomerization of styrene derivatives by CdS powder in CH₂Cl₂ solution, Mayo et al.⁹ have proposed a radical cation intermediate mechanism. Yanagida et al.¹⁰ have found that the photocatalytic cis-trans isomerization of alkenes on ZnS and CdS in aqueous methanol solutions is very efficient by aiding of sulfur radicals on the surface.

The photocatalytic hydrogenations of alkenes and alkynes with water have been investigated with TiO_2 , $^{11-14}$ TiO_2 anchored onto

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porous Vycor glass,¹⁵ Ti-Si binary oxides,^{6,16} Pt-loaded TiO₂,¹⁷ bimetal-deposited TiO₂,¹⁸ and CdS loaded with Pt or Rh.¹⁹ It was found from these results that the major photocatalytic hydrogenation products over TiO₂ are alkanes formed by the hydrogenation accompanied by the fission of the C—C or C—C bond and the photoformed e⁻(Ti³⁺ or H)-h⁺(OH) pairs at close range play a decisive role for the hydrogenolysis.^{13,17} It was also found that with metal-loaded TiO₂ the hydrogenation without bond fission is markedly enhanced owing to the addition to the π bond of the reactant of hydrogen atoms formed on metal.¹⁷⁻¹⁹

From these results, the basic factors governing the photocatalytic isomerization and hydrogenation reactions became clear to a certain extent. However, the definite explanations for the reaction mechanisms are not sufficient at present. Meanwhile, 2-butene is available for both reactions of the photocatalytic isomerization and hydrogenation. In this work, therefore, the photocatalytic isomerization and hydrogenation of *cis*-2-butene over TiO_2 and water-adsorbed TiO_2 were investigated to elucidate more detailed mechanisms for these reactions.

Experimental Section

cis-2-Butene obtained from Takachiho Kagakukogyo Co. was 99.6% pure and purified before use by condensation and evacuation at 77 K. TiO₂ catalyst was prepared by drying at 373 K the precipitate formed by adding aqueous ammonia to an aqueous solution of TiCl₄, reducing to powder with a mortar, and calcinating at 773 K for 3 h in air.²⁰ The TiO₂ catalyst had anatase structure with a mean crystalline size of 18 nm.

A high-pressure mercury lamp of 100 W (Toshiba, SHL-100UV) was used as a light source. The incident light intensity was controlled with screens. The reaction cell was a quartz cylinder of 50 mm inner diameter and 10 mm length. The volume of reaction system including the cell was 26.5 mL.

Prior to the experiment, 500 mg of TiO₂ catalyst which had been spread in the reaction cell was heated at 773 K for 1 h in the presence of O₂ and was well evacuated at the same temperature. The photocatalytic isomerization was carried out by introducing *cis*-2-butene of 4.0 kPa into the reaction cell immersed in a water bath maintained at 293 K and by irradiating with UV light. The thermal isomerization of *cis*-2-butene was also performed by the same procedure under dark conditions. The water-adsorbed TiO₂ catalyst was prepared by introducing water vapor on TiO₂ and evacuating at the room temperature. The photocatalytic hydrogenation was carried out by introducing *cis*-2-butene of 4.0 kPa on the water-adsorbed TiO₂ and by irradiating UV at 293 K.

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

Results

The adsorption of *cis*-2-butene on TiO₂ of 500 mg was measured as a function of the pressure at 293 K and it was found that the irreversible and reversible adsorption amounts are 19.9 and 47.3 μ mol at 4.0 kPa, respectively. The irreversible adsorption amount of water vapor on 500 mg of TiO₂ was 128.5 μ mol at 293 K. The reversible adsorption amount of *cis*-2-butene on the water-adsorbed TiO₂ at 4.0 kPa and 293 K was 25.4 μ mol. In this case, no

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Figure 1. Mole fraction of 1-butene of butenes measured as functions of the reaction time and the light intensity on the photocatalytic isomerization of *cis*-2-butene over TiO_2 at 293 K: relative light intensity (\bullet) 1.00; (\bullet) 0.657; (\circ) 0.208; (\bullet) 0.068; (\bullet) 0.014; (\bullet) 0.0047.



Figure 2. Mole fraction of *trans*-2-butene of butenes measured as functions of the reaction time and the light intensity on the photocatalytic isomerization of *cis*-2-butene over TiO_2 at 293 K: relative light intensity (\bullet) 1.00; (\bullet) 0.657; (\odot) 0.208; (\bullet) 0.068; (\bullet) 0.014; (\bullet) 0.0047.



Figure 3. Light intensity dependences of the initial formation rates and the initial rate ratio on the photocatalytic isomerization of cis-2-butene over TiO₂: (O) $R^0(trans-2-C_4H_8)$; (\bullet) $R^0(1-C_4H_8)$; (\bullet) $R^0(1-C_4H$

irreversible adsorption was found.

The reaction products on the photocatalytic isomerization of cis-2-butene over TiO₂ were 1-butene and *trans*-2-butene. The mole fraction of 1-butene of the total butene, measured as functions of the reaction time and the relative light intensity, is shown in Figure 1. The results for *trans*-2-butene are shown in Figure 2. It is found from Figures 1 and 2 that the conversion

TABLE I: Formation Amounts of Hydrocarbons as Functions of the Relative Light Intensity and the Reaction Time on the Photocatalytic Reaction of cis-2-Butene over Water-Adsorbed TiO_2

		formation amount, 10 ⁻⁸ mol				
I _r	t, min	CH₄	C_2H_6	<i>n</i> -C ₄ H ₁₀	$1-C_4H_8$	trans-2-C ₄ H ₈
1.000	6	0.48	8.2	1.31	67	65
	20	2.14	25.6	3.69	167	140
	40	3.99	49.3	6.18	218	213
	60	5.00		8.37	291	246
0.657	10	0.40	8.7	1.70	94	102
	22	1.00	21.2	3.49	197	189
	40	1.95	35.4	5.64	270	239
	80	3.46	56.3	9.25	397	410
0.456	10	0.25	6.3	1.26	80	73
	25	0.77	17.4	3.27	182	136
	50	1.75	31.2	5.57	284	201
	100	3.68	56.5	8.96	410	293
0.208	18	0.27	5.2	0.98	86	88
	41	0.71	13.2	2.27	163	149
	70	1.35	22.3	3.90	241	205
	120	2.29	41.6	5.59	335	239
0.068	18	0.090	2.9	0.59	58	62
	40	0.26	8.0	1.79	119	117
	70	0.58	14.3	3.10	183	169
	120	1.09	25.9	4.56	264	219

rate to *trans*-2-butene decreases more rapidly than that to 1-butene with an increase of the reaction time. This trend may be because the succeeding reactions from *trans*-2-butene to *cis*-2-butene and 1-butene take place, though the photocatalytic isomerization of 1-butene to 2-butenes proceeds scarcely.^{1,2}

The thermal isomerization rates to 1-butene and *trans*-2-butene of *cis*-2-butene over TiO₂ at 293 K were 3.4×10^{-11} and 1.2×10^{-10} mol s⁻¹, respectively. Therefore, the net photocatalytic isomerization rate was obtained by subtracting the thermal isomerization rate from the total isomerization rate showed in Figure 1 or 2. The initial rate by the net photocatalytic reaction (R^0) was estimated by extrapolating to t = 0 the plot of V/t versus t, where V denotes the amount of product formed at reaction time t. The net initial isomerization rates to 1-butene and *trans*-2butene and the net initial rate ratio of $R^0(1-C_4H_8)/R^0(trans-2-C_4H_8)$ are shown in Figure 3 as a function of the relative light intensity.

The hydrocarbon products formed by the photocatalytic reaction of *cis*-2-butene over water-adsorbed TiO₂ were CH₄, C₂H₆, *n*-C₄H₁₀, 1-butene, and *trans*-2-butene, where their thermal formations were not found at 293 K. The formation amounts of these products (V) are shown in Table I as functions of the relative light intensity (I_r) and the reaction time (t). The initial formation rate (R^0) was estimated by extrapolating to t = 0 the plot of V/t or t/V versus t. The values of R^0 as a function of I_r are shown in Figure 4. It is found that the initial formation rates of CH₄, C₂H₆, and n-C₄H₁₀ are in proportion to the first order of the relative light intensity. Meanwhile, trace formation of C₃H₈ was found, though the initial formation rate is zero. The same trend for C₃H₈ was also found in the photocatalytic hydrogenation of *trans*-2butene on water-adsorbed TiO₂.

Discussion

Light Intensity Dependence. By irradiation of UV light to TiO₂, which is a semiconductor, the electron in the conduction band and the positive hole in the valence band are formed. When the photoformed electron (e^-) and positive hole (h^+) are trapped into Ti⁴⁺ and O²⁻ ions of TiO₂, Ti³⁺ and O⁻ are formed.²¹

$$(TiO_2) + h\nu \rightarrow h^+ + e^-$$
(1)

$$e^- + Ti^{4+} \rightarrow Ti^{3+}$$
(2)

$$h^+ + O^{2-} \to O^- \tag{3}$$



Figure 4. Light intensity dependences of the initial formation rates on the photocatalytic reaction of *cis*-2-butene over water-adsorbed TiO₂ at 293 K: (\bigcirc) *trans*-2-C₄H₈; (\bigcirc) 1-C₄H₈; (\bigcirc) C₂H₆ (×7); (\bigcirc) *n*-C₄H₁₀ (×20); (\bigcirc) CH₄ (×50).

When H⁺ and OH⁻ ions exist on the surface of TiO₂,²² H atoms and OH radicals are formed as the results that the photoformed electrons and holes are trapped into these ions.^{17,22}

$$e^- + H^+ \to H \tag{4}$$

$$h^+ + OH^- \rightarrow OH$$
 (5)

However, almost all of the photoformed electrons and positive holes disappear by the recombination reaction²³

$$h^+ + e^- \rightarrow \text{thermal energy}$$
 (6)

because the quantum yields for the photocatalytic isomerization and hydrogenation are very low. $^{\rm 24}$

On the steady-state assumption, the formation rate of holes or electrons is equal to the number of photons absorbed per unit time; that is, it is in proportion to the relative light intensity (I_r) . Meanwhile, the disappearance rate of holes or electrons is approximately proportional to the product of the concentration of holes ([h⁺]) and the concentration of electrons ([e⁻]), because the greater parts of holes and electrons disappear by reaction 6. From these relations, the equations

$$d[h^{+}]/dt = d[e^{-}]/dt = aI_{r}$$
$$= k_{r}[h^{+}][e^{-}]$$
(7)

are formed, where a and k_r mean the proportional constant for the light absorption and the recombination rate constant.

It is possible to assume $[h^+] = [e^-]$, because the disappearances of h^+ and e^- by reactions 2-5 are negligible as compared with those by reaction 6. Then, the equation

$$[h^+] = [e^-] = bI_r^{1/2}$$
 (8)

can be derived from eq 7, where $b = (a/k_r)^{1/2}$. The formation rates of Ti³⁺, O⁻, H, and OH by reactions 2–5 are also proportional to [h⁺] or [e⁻] and hence $I_r^{1/2}$, because the concentrations of Ti⁴⁺, O²⁻, H⁺, and OH⁻ on the surface of TiO₂ are constant in the initial stage of reaction. These relations suggest the following findings: the rate of the reaction in which one species of Ti³⁺, O⁻, H, or

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Figure 5. Plots of $\mathbb{R}^0/I_r^{1/2}$ versus $I_r^{1/2}$ on the photocatalytic isomerization of *cis*-2-butene over TiO₂ at 293 K: (\bullet) 1-butene; (O) *trans*-2-butene.

TABLE II: Light Intensity Dependence of the Initial Rates of the Photocatalytic Reactions of cis-2-Butene over TiO₂ and Water-Adsorbed TiO₂

catalyst	product	$\alpha(I_r),$ nmol s ⁻¹	$\beta(I_r^{1/2}),$ nmol s ⁻¹
TiO ₂	1-C ₄ H ₈	6.09	1.21
-	trans-2-C ₄ H ₈	3.39	3.35
water-adsorbed TiO ₂	CH₄	0.0087	0
	C ₂ H ₆	0.236	0
	$n-C_4H_{10}$	0.045	0
	1-C ₄ H ₈	0	2.23
	trans-2-C ₄ H ₈	0	2.45

OH participates independently is proportional to $I_r^{1/2}$; the rate of the reaction in which two species of Ti³⁺, O⁻, H, and OH are concerned cooperatively is in proportion to the first order of I_r .

For the photocatalytic isomerizations of cis-2-butene over TiO₂, the plots of $R^0/I_r^{1/2}$ versus $I_r^{1/2}$ are shown in Figure 5. When the initial rate is expressed by the general form

$$R^0 = \alpha I_r + \beta I_r^{1/2} \tag{9}$$

the values of α and β obtained from the slopes and the intercepts in Figure 5 are shown in Table II.

For the photocatalytic reactions over water-adsorbed TiO₂, plots of R^0 versus $I_r^{1/2}$ for the formations of 1-butene and *trans*-2-butene are shown in Figure 6. The values of β obtained from the slopes are also shown in Table II together with the values of α obtained from the slopes of Figure 4 for the formations of CH₄, C₂H₆, and n-C₄H₁₀.

Reactions Mechanisms for the Photocatalytic Isomerizations. On the photocatalytic isomerizations of cis-2-butene, reaction modes of four kinds are conceivable, because both the isomerizations to 1-butene and trans-2-butene have the α and β reaction modes.

For the photocatalytic isomerization to *trans*-2-butene by the α -type, the following scheme was postulated:

SCHEME I

$$\begin{array}{c} (1) \\ CH_{3}-CH=CH-CH_{3} \\ \hline \\ CH_{3}-CH=CH-CH_{3} \\ \hline \\ (1) \\ CH_{3}-CH=CH_{3} \\ \hline \\ (1) \\ (1) \\ (1) \\ CH_{3}-CH=CH_{3} \\ \hline \\ (1) \\$$

The sequences of reaction are as follows: (1) addition of \dot{O}^- to C(2); (2) electron transfer from $\dot{C}(3)$ to O^- and internal rotation about the C(2)–C(3) axis; (3) electron transfer from $\dot{T}i^{3+}$ to C⁺(3); (4) desorption of *trans*- or *cis*-2-butene.

This scheme was proposed for the following reasons: the isomerization does not proceed on water-adsorbed TiO_2 which Ti^{4+}



Figure 6. Plots of R^0 versus $I_r^{1/2}$ on the photocatalytic isomerization of *cis*-2-butene over water-adsorbed TiO₂ at 293 K: (\bullet) 1-butene; (O) *trans*-2-butene.

and O^{2-} are actually absent on the surface; Ti^{3+} and \dot{O}^{-} existing at a close range participate cooperatively because of the α -type isomerization; the cation intermediate II is easier than the radical intermediate I for the internal rotation about the C(2)-C(3) axis, because the internal rotation in the radical intermediate I is difficult by the formation of a bridged type π complex.²⁵



The cis-trans isomerization mechanisms by cationic intermediates were also proposed by Morikawa et al.⁸ and Mayo et al.⁹

The α -type photocatalytic isomerization to 1-butene seems to proceed by the previously proposed mechanism.³

SCHEME II

The sequences on the isomerization are as follows: (1) addition of Ti^{3+} to C(2); (2) H⁺ abstraction from OH⁻(O²⁻-H⁺) by C(3); (3) electron transfer from Ti^{3+} to C⁺(3); (4) hydrogen abstraction from methyl group (C(1)) by O⁻ which is an anion radical;²⁶ (5) desorption of 1-butene. This scheme was postulated for the reasons that the α -type isomerization does not proceed on water-adsorbed TiO₂ and the shift of hydrogen is required for the double bond migration. The existence of surface OH groups on TiO₂ evacuated at 773 K has been well-known.²⁷

For the β -type isomerization to *trans*-2-butene, the mechanism in Scheme III was presumed. The sequences for the isomerization are as follows: (1) addition of $\dot{O}H$ to C(2); (2) hydrogen abstraction from OH by $\dot{C}(3)$ and internal rotation about the C-(2)-C(3) axis; (3) hydrogen abstraction by \dot{O} from CH₂(C(3)); (4) desorption of *trans*- or *cis*-2-butene by the injection of an electron.

The β -type isomerization to *trans*-2-butene proceeds over TiO₂ and water-adsorbed TiO₂. However, Ti⁴⁺ and O²⁻ are actually

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SCHEME IV



absent on the surface of water-adsorbed TiO₂. The reaction of cis-2-butene with H atoms leads to the hydrogenation product, $n-C_4H_{10}$. Thus, only OH radicals seem to be available for the isomerization. Meanwhile, the internal rotation about the C-(2)-C(3) axis of the radical intermediate III is difficult, because the bridged type π complex

is formed. For these reasons, Scheme III was presumed.

From the same viewpoint as Scheme III, the mechanism in Scheme IV was postulated for the β -type isomerization to 1-butene. Scheme IV is different from Scheme III in that the hydrogen abstraction from CH₃(C(1)) by O in the intermediate IV proceeds in place of the hydrogen abstraction from CH₂(C(3)).

On the photocatalytic isomerization of $cis-2-C_4H_8$ over D_2O adsorbed TiO₂ (Degussa, P-25) evacuated at 453 K, it was found that the deuterium contents in 1-butene (mole fraction 0.554), cis-2-butene (0.234), and trans-2-butene (0.212) after reaction are 11.2, 3.7, and 3.0%, respectively.² The D content in 1-butene is considerably high as compared with those in 2-butenes. The result is explainable by the following reasons: the H-D exchange by Scheme I cannot be expected; the probability of the H-D exchange by Scheme III is about one-half; the probability by Schemes II and IV is expected to be unity. It was also found that almost all of surface D atoms which are available for the photocatalysis are consumed by the H-D exchanges. Therefore, the H-D exchanges seem to be very effective. These results are strongly supported Schemes I-IV. Moreover, the photoisomerization rates to 1-butene and trans-2-butene over the D2O-adsorbed TiO_2 were quite the same as those over H₂O-adsorbed TiO_2 pretreated under the same conditions.² The result is suggested that the H-D exchange processes in Schemes II-IV are not rate-determining steps.

Reaction Mechanisms for the Photocatalytic Hydrogenolysis and Hydrogenation. On the photocatalytic reactions of cis-2butene over water-adsorbed TiO₂, Ti³⁺ and O⁻ are not available as described above. The addition of H atoms to cis-2-butene leads to the formation of n-C₄H₁₀. Thus, the mechanism in Scheme V was postulated for the formation of CH₄ by the α -type hydrogenolysis. The reaction sequences are as follows: (1) additions of OH to C(2) and H to C(3); (2) weakening of the C(1)-C(2)



SCHEME VI

$$CH_{3}-CH=CH-CH_{3} \xrightarrow{(1)} CH_{3}-CH-CH_{2}-CH_{3} \xrightarrow{(2)}$$

$$\dot{O}H \stackrel{\dot{H}}{H} \xrightarrow{(V)}$$

$$CH_{3}-CH-CH_{2}-CH_{3} \xrightarrow{(3)} CH_{3}-CH=O(ads) + C_{2}H_{6}$$

SCHEME VII

$$\begin{array}{c} CH_{2} \equiv CH - CH_{2} - CH_{3} \xrightarrow{(1)} CH_{2} - CH_{2} - CH_{2} - CH_{3} \xrightarrow{(2)} \\ \downarrow \\ O - H \\ CH_{2} - CH_{2} - CH_{2} - CH_{3} \xrightarrow{(3)} CH_{2} \equiv O(ads) + C_{3}H_{8} \\ \downarrow \\ O - H \\ \end{array}$$

bond and strengthening of the C(2)-O bond; (3) formations of CH_4 and CH_3 — CH_2 —CH=O(ads) on the catalyst surface.

Process 1 of Scheme V is exothermic with 543 kJ when the standard heats of formation in the gas phase are applied for H, OH, *cis*-2-butene, and *s*-C₄H₉OH.²⁸ The bond dissociation energy of the C(1)-C(2) bond in the intermediate V is about 360 kJ. Therefore, the formations of CH₄ and C₂H₅CHO(ads) resulting from the weakening of the C(1)-C(2) bond and the strengthening of the C(2)-O bond seem to be energetically possible. A similar mechanism has been proposed for the formation of aldehydes by the strengthening of C-O bond on the photoinduced metathesis reaction of alkenes over MoO₃.²⁹

From the same standpoint as Scheme V, the mechanism in Scheme VI was presumed for the formation of C_2H_6 by the α -type hydrogenolysis. This scheme is different from Scheme V in that the C(2)-C(3) bond of the intermediate V weakens instead of the C(1)-C(2) bond.

The direct formation of C_3H_8 from the intermediate V of Scheme V or VI is not conceivable. Namely, the trace formation of C_3H_8 by a secondary reaction seems to result from 1-butene formed by Scheme IV. Thus, the mechanism in Scheme VII was presumed from the same conceptions as those in Schemes V and VI. This mechanism is supported by the results that the amount of C_3H_8 formed as a secondary product is about 1/300 of that of 1-butene and C_3H_8 is formed with high yield ($R^0 = 0.25$ nmol s⁻¹) as a primary product in the photocatalytic hydrogenation of 1-butene over water-adsorbed TiO₂.³⁰

For the formation of $n-C_4H_{10}$ by the α -type hydrogenation, the mechanism

SCHEME VIII

$$\begin{array}{c} \mathsf{CH}_3 \longrightarrow \mathsf{CH}_{\square} \mathsf{CH}_3 \longrightarrow \mathsf{PC}_4 \mathsf{H}_{10} \\ \dot{\mathsf{H}} & \dot{\mathsf{H}} \end{array}$$

was postulated in the same way as the reaction of C_2H_4 + 2H

⁽²⁸⁾ Calvert, J. G.; Pitts, J. N. Photochemistry; Wiley: New York, 1967; p 815.

⁽²⁹⁾ Anpo, M.; Tanahashi, I.; Kubokawa, Y. J. Chem. Soc., Faraday Trans. 1 1982, 78, 2121. Kubokawa, Y.; Anpo, M. In Adsorption and Catalysis on Oxide Surfaces; Che, M., Bond, G. C., Eds.; Elsevier: Amsterdam, 1985; p 127.

⁽³⁰⁾ We have also investigated for the photocatalytic reactions of C_2H_2 , C_2H_4 , $CH_3C \equiv CH$, C_3H_6 , 1,3-butadiene, 1-butene, *trans*-2-butene, and isobutene over water-adsorbed TiO₂.

→ C_2H_6 which was proposed by Baba et al.¹⁸ The formation of $n-C_4H_{10}$ by the reactions $H + C_4H_8 \rightarrow C_4H_9$ and $C_4H_9 + H \rightarrow n-C_4H_{10}$ or $C_4H_9 + OH^- \rightarrow n-C_4H_{10} + O^-$ is not conceivable for the reasons that the rate of formation of $n-C_4H_{10}$ by these reactions is not proportional to I_r and the alkyl radicals on catalyst surface disappear in general by the recombination and cross-combination reactions without react with the surface OH and OH⁻ groups.^{26,31}

On the photocatalytic hydrogenations of C_2H_4 and C_3H_6 with D_2O over TiO₂ (Degussa, P-25), it was found that the CH_2D_2 content in methanes is excessively high.¹³ It may be because CH_2D_2 is formed via the addition intermediates

in common with Schemes V–VII. This result is strongly sustained by the mechanisms of Schemes V–VII. It was also found that all of the formation mechanisms of hydrocarbons produced by the photocatalytic hydrogenolysis and hydrogenation of unsaturated hydrocarbons over water-adsorbed TiO₂ can be explained by the basic conceptions stated in Schemes V–VIII.³⁰

Comparisons of Initial Rates. The rate of formation of C_2H_6 resulting from the fission of the C(2)-C(3) bond of the intermediate V is 27 times faster than that of CH₄ arising from the fission of the C(1)-C(2) bond, although their formation mechanisms are partly common as are seen in Schemes V and VI. A reason for the fact may be because the bond dissociation energy of the C(2)-C(3) bond is lower than that of the C(1)-C(2) bond.³²

The total yield of CH_4 and C_2H_6 arising from OH and H is 5.4 times higher than the yield of n- C_4H_{10} resulting from two H atoms. This may be caused by the fact that the addition of OH to *cis*-2-butene is much faster than that of H; that is, the addition rate constants of OH and H to *cis*-2-butene in the vapor phase at 25 °C are 54.7³³ and 1.05³⁴ in 10⁻¹² mL molecule⁻¹ s⁻¹ units, respectively.

The photocatalytic isomerizations to 1-butene and *trans*-2butene over water-adsorbed TiO_2 are much faster than the hydrogenolyses to CH_4 and C_2H_6 . The fact is suggested that the probability that OH and H pairs at close range act cooperatively is low, although the addition to *cis*-2-butene of OH participating in the isomerizations is very fast.

As mentioned above, cis-2-C₄H₇D of 3.7% together with *trans*-2-C₄H₇D of 3.0% were found on the photocatalytic isomerization of cis-2-C₄H₈ over D₂O-adsorbed TiO₂.² Therefore, if we assume that the formation amount of cis-2-butene by Scheme III is nearly the same as that of *trans*-2-butene, it leads to the result that the hydrogen abstraction rate from CH₂(C(3)) by O in the intermediate IV of Scheme III or IV is about 2 times faster than that from CH₃(C(1)), judging from the isomerization rates over water-adsorbed TiO₂. This result agrees with the finding that the abstraction rate of a secondary hydrogen from CH₂ group is faster than that of a primary hydrogen from CH₃ group, as were generally found on the hydrogen abstractions by radical species in the vapor phase.³⁵

The ratio of $R^0(trans-2-C_4H_8)/R^0(1-C_4H_8)$ by the β -type isomerizations on TiO₂ is 2.5 times larger than that on wateradsorbed TiO₂. This result suggests that the internal rotation about the C(2)-C(3) axis of the intermediate IV on TiO₂ is easier as compared with that on water-adsorbed TiO₂, because of less steric hindrance by the absence of adsorbed water.

The sum of initial rates of the β -type isomerizations by OH on TiO₂ is about one-half of that of the α -type isomerizations by Ti³⁺ and O⁻ on TiO₂ and is nearly the same as that of the β -type isomerizations by OH on water-adsorbed TiO₂, though the concentration of surface OH⁻ on TiO₂ is much less than that on water-adsorbed TiO₂. These results suggest that the capture of positive holes into surface OH⁻ isolated on TiO₂ is very effective.

Summary

The photocatalytic isomerizations to 1-butene and *trans*-2butene, hydrogenolyses to CH_4 and C_2H_6 , and hydrogenation to $n-C_4H_{10}$ proceed under UV irradiation of water-adsorbed TiO₂ with *cis*-2-butene, though only the isomerizations occur on TiO₂. The total yield of the isomerizations on TiO₂ proceeding by four reaction mechanisms was 48.5 times higher than that of CH_4 , C_2H_6 , and $n-C_4H_{10}$ forming on water-adsorbed TiO₂ at $I_r = 1$. The reaction mechanisms that Ti³⁺-O⁻ pair, Ti³⁺-O⁻ pair and OH⁻, or OH radical for the isomerizations, OH-H pair for the hydrogenolyses, and two H atoms for the hydrogenation are concerned in their formations were presumed.

Registry No. CH₄, 74-82-8; C₂H₆, 74-84-0; *n*-C₄H₁₀, 106-97-8; 1-C₄H₈, 106-98-9; *trans*-2-C₄H₈, 624-64-6; *cis*-2-C₄H₈, 590-18-1; C₃H₈, 74-98-6; TiO₂, 13463-67-7.

⁽³¹⁾ Kraeutler, B.; Bard, A. J. J. Am. Chem. Soc. 1978, 100, 5985. Yoneyama, H.; Takao, Y.; Tamura, H.; Bard, A. J. J. Phys. Chem. 1983, 87, 1417.

⁽³²⁾ The bond dissociation energy of the C(2)-C(3) bond of the intermediate V was estimated to be 12.5 kJ mol⁻¹ lower than that of the C(1)-C(2) bond, when the bond dissociation energy of the CH₃CH(OH)-H bond is assumed to be equal to that of the C₂H₃CH(OH)-H bond and the standard heats of formation in the vapor phase of 143.9, 107.5, -235.1, -259.0, and -293.3 kJ mol⁻¹ are applied for CH₃, C₂H₅OH, *n*-C₃H₇OH, and *s*-C₄H₉OH, respectively.

⁽³³⁾ Ohta, T. Int. J. Chem. Kinet. 1984, 16, 879.

⁽³⁴⁾ Kyogoku, T.; Watanabe, T.; Tsunashima, S.; Sato, S. Bull. Chem. Soc. Jpn. 1983, 56, 19.

⁽³⁵⁾ Trotman-Dickenson, A. F. Gas Kinetics; Butterworths: London, 1955; p 224.