

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 way.

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_2

Sukeya Kodama* and Shinji Yagi

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan (Received: July 11, 1989; In Final Form: November 14, 1989)

Photocatalytic reactions of 1,3-butadiene over water-adsorbed TiO_2 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 $\mu\text{mol s}^{-1}$, respectively. The formations of CH_4 , *n*- C_4H_{10} , CO, *n*- $\text{C}_3\text{H}_7\text{CHO}$, *s*- $\text{C}_4\text{H}_9\text{OH}$, and *n*- $\text{C}_4\text{H}_9\text{OH}$ were also observed. The drastic decrease of the hydrocarbon yields by the addition of O_2 was not found except for C_2H_6 and C_3H_8 . The increase of formation yield by the loading of Pt was observed for all products, especially *n*- C_4H_{10} . 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_2 ,^{1–5} TiO_2 and TiO_2 -doped Fe_2O_3 ,⁶ TiO_2 anchored onto porous Vycor glass,⁷ Ti-Si⁸ and Ti-Al⁹ binary oxides, metal-loaded TiO_2 ,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}

Recently, the yields of products formed by the photocatalytic reactions of *cis*-2-butene over water-adsorbed TiO_2 were observed as a function of the irradiation time and the incident light intensity.¹² It was found that the initial formation rates of CH_4 and C_2H_6 formed by the hydrogenolysis reaction and *n*- C_4H_{10} 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_2 .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_2 may be considerably different from those for alkenes such as *cis*-2-butene. Previously, it was reported that C_3H_6 , C_3H_8 , and trace CH_4 are formed by the photocatalytic reactions of 1,3-butadiene.² However, the details for the reaction mechanisms are not clear. Thus, the photocatalytic reactions of 1,3-butadiene over water-adsorbed TiO_2 were in-

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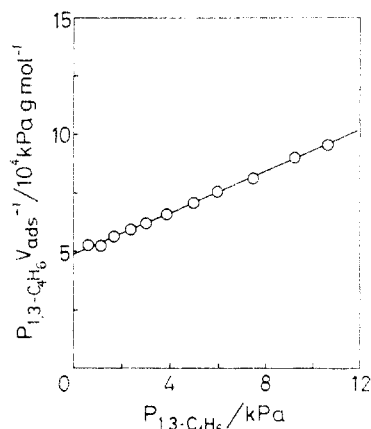


Figure 1. Plot of $P_{1,3-C_4H_6} V_{ads}^{-1}$ versus $P_{1,3-C_4H_6}$ for the adsorption isotherm of 1,3-butadiene on water-adsorbed TiO_2 at 293 K.

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_2 catalyst was prepared by drying at 373 K the precipitate formed by adding aqueous ammonia to an aqueous solution of $TiCl_4$, calcinating at 773 K for 3 h in air, and reducing to powder with a mortar.¹⁴

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 TiO_2 catalyst that had been spread in the reaction cell was heated at 773 K for 1 h in the presence of 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 $36.4 \text{ m}^2 \text{ g}^{-1}$ from the BET method by supposing that the area of N_2 molecule as an adsorbate is 16.2 \AA^2 .¹⁵ The irreversible adsorption amount of water vapor on TiO_2 was $4.25 \text{ molecules nm}^{-2}$ 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

$$\frac{P}{V_{ads}} = \frac{k_1/k_2}{V_{max}} + \frac{P}{V_{max}} \quad (1)$$

for the adsorption isotherm,¹⁶ the relation of $P_{1,3-C_4H_6}/V_{ads}$ versus $P_{1,3-C_4H_6}$ 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 $k_1/k_2 = 11.2 \text{ kPa}$ and $V_{max} = 3.77 \text{ molecules nm}^{-2}$ 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_2

product	formation amount, nmol		
	TiO_2^a	O_2/TiO_2^b	Pt/TiO_2^c
CH_4	13	14	27
C_2H_4	25	81	36
C_2H_6	22	1	50
C_3H_6	507	760	836
C_3H_8	613	2	1096
1- C_4H_8	385	39	619
<i>trans</i> -2- C_4H_8	86	21	236
<i>n</i> - C_4H_{10}	9	3	127

^a TiO_2 without O_2 . ^b TiO_2 with O_2 (1.7 kPa). ^c TiO_2 loaded with Pt (4 wt %).

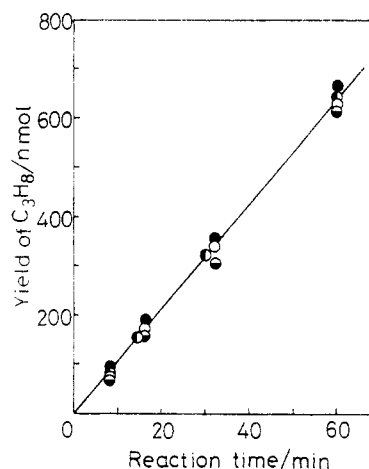


Figure 2. Formation yield of C_3H_8 measured as functions of the pressure of 1,3-butadiene and the irradiation time on the photocatalytic reaction over water-adsorbed TiO_2 : pressure of 1,3-butadiene (●) 2.0 kPa; (○) 4.0 kPa; (◐) 8.0 kPa; (◑) 13.3 kPa.

The hydrocarbon products formed by the photocatalytic reactions of 1,3-butadiene over water-adsorbed TiO_2 were CH_4 , C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , 1-butene, *trans*-2-butene, and *n*- C_4H_{10} . These products were also found in the photocatalytic reactions on water-adsorbed TiO_2 with O_2 of 1.7 kPa (O_2/TiO_2) and on water-adsorbed TiO_2 loaded with 4 wt % Pt black without the O_2 pretreatment at 773 K (Pt/TiO_2). 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_7CHO , *s*- C_4H_9OH , and *n*- C_4H_9OH 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 time¹² and are shown in Table II.

Meanwhile, it is found in Figure 4 that the formation yield of *n*- 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_4 . These results suggest that CH_4 and *n*- C_4H_{10} are not formed as a primary product.

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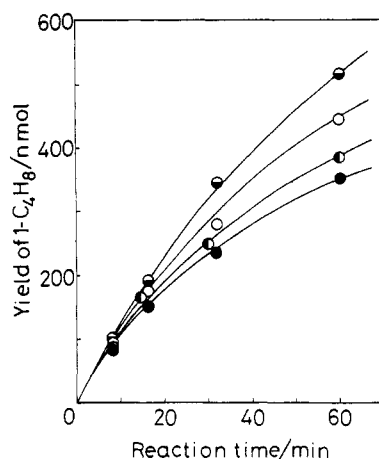


Figure 3. Formation yield of 1-butene observed as functions of the pressure of 1,3-butadiene and the irradiation time on the photocatalytic reaction over water-adsorbed TiO_2 : pressure of 1,3-butadiene (●) 2.0 kPa; (◐) 4.0 kPa; (○) 8.0 kPa; (⊗) 13.3 kPa.

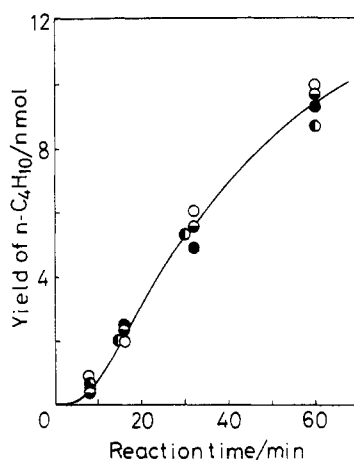


Figure 4. Formation yield of $n\text{-C}_4\text{H}_{10}$ measured as functions of the pressure of 1,3-butadiene and the reaction time on the photocatalytic reaction over water-adsorbed TiO_2 : pressure of 1,3-butadiene (●) 2.0 kPa; (◐) 4.0 kPa; (○) 8.0 kPa; (⊗) 13.3 kPa.

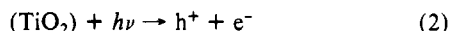
TABLE II: Initial Formation Rate of the Products Formed by the Photocatalytic Reaction of 1,3-Butadiene over Water-Adsorbed TiO_2 and Enthalpy Change of the Reactions in Schemes I–V

product	R^0 , pmol s^{-1}	ΔH_{298}° , kJ mol^{-1}
C_2H_4	8.1	-480.9
C_2H_6	7.1	-512.4
C_3H_6	267	-462.5
C_3H_8	177	-581.5
1- C_4H_8	209	-546.3
<i>trans</i> -2- C_4H_8	34	-557.3

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

Discussion

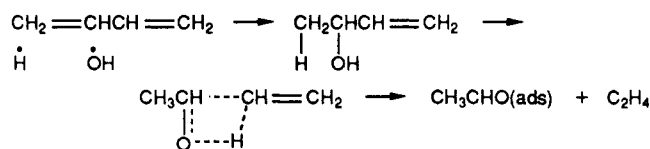
Reaction Mechanisms. By irradiation of UV light to TiO_2 , which is a semiconductor, the electron (e^-) in the conduction band and the positive hole (h^+) in the valence band are formed:



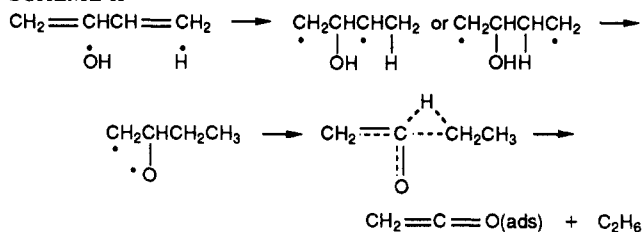
When H^+ and OH^- ions exist on the surfaces of TiO_2 , H atoms and OH radicals are formed because the photoformed electrons and holes are trapped into these ions:^{4,17}



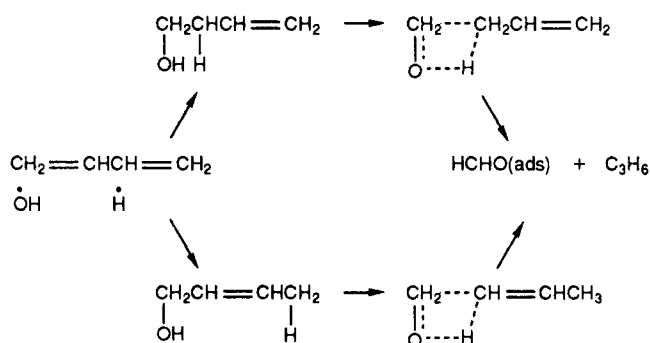
SCHEME I



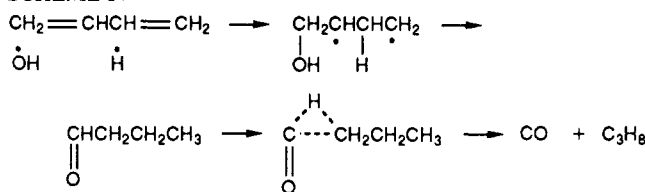
SCHEME II



SCHEME III



SCHEME IV



In previous work,¹² the reaction mechanisms proceeding by additions to the π bonds of the OH radical and H atom at close range were proposed for the formations of CH_4 and C_2H_6 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 water-adsorbed TiO_2 ,¹³ the reaction mechanisms for the formations of C_2H_4 , C_2H_6 , C_3H_6 , and C_3H_8 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 $n\text{-C}_3\text{H}_7\text{CHO}$ is found; CO of nearly the same amount as C_3H_8 is formed.

The initial formation rate of CH_4 is zero, though the yield increases quickly with an increase of the irradiation time, similarly as the trend for $n\text{-C}_4\text{H}_{10}$ in Figure 4. Therefore, the formation of CH_4 seems to arise from subsequent hydrogenolyses of $\text{CH}_3\text{CHO(ads)}$, $\text{CH}_2=\text{C}=\text{O(ads)}$, C_2H_4 , C_3H_6 , and butenes formed by the photocatalytic reactions of 1,3-butadiene.^{12,13}

In the light of the mechanism for the photocatalytic hydrogenations of C_2H_4 ¹¹ and *cis*-2-butene,¹² Scheme V was postulated

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TABLE IV: Frontier Electron Densities and Charge Distribution on Each Position of the $\text{CH}_2\text{---CH---CH---CH}_3$ Radical

position	$f_r^{(E)}$	$f_r^{(N)}$	$f_r^{(R)}$	q_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_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_3H_4 and C_2H_6 result from the addition of OH to the C(2) position of 1,3-butadiene and that C_3H_6 and C_3H_8 are derived from the addition of OH to the C(1) position. Then, the rate ratio

$$(R^\circ_{\text{C}_3\text{H}_6} + R^\circ_{\text{C}_3\text{H}_8}) / (R^\circ_{\text{C}_2\text{H}_4} + R^\circ_{\text{C}_2\text{H}_6}) = 29.2$$

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 $\text{CH}_2=\text{CHCH}_3$, $\text{CH}_2=\text{C}(\text{CH}_3)_2$, and $\text{CH}\equiv\text{CCH}_3$ over water-adsorbed TiO_2 .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.²³ 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,²⁴ the reactive position in a radical for the electrophilic, nucleophilic, and radical attack reactions can be estimated from the frontier electron densities:

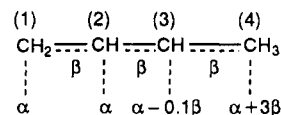
$$f_r^{(E)} = (c_r^{\text{ho}})^2 + (c_r^{\text{so}})^2 \quad (6)$$

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

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

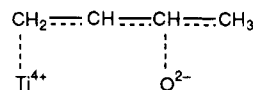
Here, $f_r^{(E)}$, $f_r^{(N)}$, and $f_r^{(R)}$ mean the electron densities for the electrophilic, nucleophilic, and radical attack reactions, respectively. c_r^{ho} , c_r^{so} , c_r^{lu} denote the coefficients of r th position of the highest occupied, singly occupied, and lowest unoccupied molecular 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_3 group:²⁵



Here, α and β 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^{4+} (or H^+) and O^{2-} (or OH^-) on the catalyst surface, respectively:



However, the interaction of C(1) and Ti^{4+} is conceivably more effective than that of C(3) with O^{2-} , judging from the values of $f_r^{(E)}$, $f_r^{(N)}$, and q_r and the numbers of charges of Ti^{4+} and O^{2-} 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^{4+} 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

$$\frac{[R^\circ_{\text{C}_2\text{H}_4} + R^\circ_{\text{C}_2\text{H}_6} + R^\circ_{\text{C}_3\text{H}_6} + R^\circ_{\text{C}_3\text{H}_8}]_{1,3\text{-butadiene}}}{[R^\circ_{\text{CH}_4} + R^\circ_{\text{C}_2\text{H}_6}]_{\text{cis-2-butene}}} = 1.9$$

The result is supported by the fact that both k_{OH} and k_H for 1,3-butadiene are larger than those of *cis*-2-butene^{26,27} 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

$$\frac{[R^\circ_{1\text{-C}_4\text{H}_8} + R^\circ_{\text{trans-2-C}_4\text{H}_8}]_{1,3\text{-butadiene}}}{[R^\circ_{n\text{-C}_4\text{H}_{10}}]_{\text{cis-2-butene}}} = 5.4$$

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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