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Photocatalytic Isomerization of Butenes over TiO_2. Photo-Formed Active Species and Characteristics of Reaction

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It has been found that UV irradiation of powdered TiO_2 catalysts in the presence of butene molecules leads to both cis-trans and double bond shift isomerization reactions with high efficiency. In the photocatalytic isomerization the reactivity of 2-butene is much higher than that of 1-butene, being in contrast to the feature in the thermal isomerization. The addition of O_2 or NO molecules leads to the complete inhibition of photocatalytic isomerization of butenes. The effect of adsorbed water on the photocatalytic isomerization has been investigated. From these results together with the ESR measurements under UV irradiation of TiO_2 at 77 K in the presence of butene as well as O_2 or NO, the following conclusion emerges: The interaction of the photo-formed O^- species or $[Ti^{3+}\text{–}O^-]$ pairs results in opening of the C=C bond of butene, i.e. formation of a radical species, which acts as the intermediate in the photocatalytic isomerization. The O^- as well as surface OH^- species participates in the hydrogen shift, i.e. the double bond shift isomerization. Thus, the reaction mechanism which has been proposed for the photocatalytic isomerization of butene over ZnO has been confirmed over TiO_2.

Photocatalysis of powdered semiconductors has received much attention from the standpoint of photochemistry of solid surfaces as well as the possibility of utilization of solar energy. However, most studies have been mainly made with the reactions associated with the photodecomposition of water over metal loaded semiconductors.[1] In order to understand the true nature of the photocatalysis, it seems necessary to investigate the photocatalytic reactions other than the oxidation and reduction reactions. As an approach along this line, a number of workers have investigated the isomerization of alkenes over metal sulfides such as CdS[2] and ZnS[3] as well as metal oxides,[4] indicating that photocatalytic isomerization reactions proceed with higher efficiency than other photocatalytic reactions such as H_2 evolution reaction from water. In these systems only the cis-trans isomerization, i.e. geometrical isomerization proceeds.

As described previously,[5] we have found out that the double bond shift isomerization as well as geometrical isomerization of butenes is markedly enhanced over TiO_2 and ZnO under UV irradiation (band gap light). We have also proposed the mechanism for photocatalytic isomerization over ZnO catalyst on the basis of detection of reaction intermediate species by using ESR.[6] However, in the case of ZnO, the isomerization proceeds significantly in the dark even at 273 K, suggesting that separation of the photocatalytic isomerization seems to be very difficult. Accordingly, in the present work, with TiO_2 where the isomerization scarcely proceeds in the dark at room temperature, we have investigated the photocatalytic isomerization by ESR techniques as well as product analysis.

Experimental

Materials. The TiO_2 was obtained from Japan Aerosil Co. (P-25, Degussa, BET surface are: 40 m^2/g, average particle size: 0.029 μm, purity: >97%). Pure rutile type TiO_2 from Ishihara Industry Co. (BET surface area: 7.5 m^2/g, average particle size: 0.1—0.2 μm). The reactant gases (1-butene, *cis*-2-butene, and *trans*-2-butene) as well as NO gases were of extra pure grade from Takachiho Kagakukogyo Co. (purity of 1-butene: >99.1%, *cis*-2-butene: >98.9%, *trans*-2-butene: >99.8%, respectively). They were used without further purification. Commercial tank oxygen was purified by low-temperature distillation. Deionized double-distilled water was degassed by alternate freezing and thawing in vacuo. Deuterium dioxide of 99.9 mol% isotopical purity (E. Merk, Darmstadt) were used without further purification.

Apparatus and Procedure. Details of the apparatus and procedure were described in our previous papers.[5,6] The quartz cell having a volume of ca. 43 cm^3 was connected to a conventional vacuum system. Ultimate vacua of 1.33×10^{-3} Pa (1×10^{-5} Torr) were attainable. The sample of 0.3 g (P-25) or 0.6 g (rutile) was subjected to oxygen treatment at 833 K, followed by evacuation at the same temperature. The TiO_2 powder was spread on the quartz cell window, having a surface area of about 32 cm^2. The reactant butene was introduced onto the catalysts, its pressure being adjusted in the range of about 4.0 kPa (30 Torr). Then UV irradiation was carried out at 313 K using a Toshiba SHL-100UV Hg lamp with a color filter (Toshiba UV-D33S; $\lambda\cong$260—420 nm) and a water filter. Analysis of the reaction products was made by gas chromatography. Isotopic analysis of butenes was carried out with Hitachi RME-6E mass spectrometer using low-voltage electrons in just sufficient amount to produce an ion of the parent mass. ESR measurements were carried out at 77 K with a JSE-ME-1 (X-band) spectrometer. Mn^{2+} ions in MgO powders were used for g-values and sweep calibration. UV irradiation for ESR measurements was carried out by using a 500 W Hg lamp with a color filter (Toshiba UV-29; $\lambda\geq$280 nm).

Results and Discussion

1. Photocatalytic Isomerization of 2-Butenes over

TiO_2. As shown in Fig. 1, UV irradiation of TiO_2 in the presence of *trans*-2-butene leads to the formation of 1-butene as well as *cis*-2-butene. The yield of 1-butene increases with UV irradiation time, while that of *cis*-2-butene passes through a maximum and then slowly decreases. The rate of 1-butene formation (double bond shift isomerization) is much larger than that of *cis*-2-butene formation (geometrical isomerization). As shown in Fig. 2, similar results were obtained with *cis*-2-butene. As described previously,[5,6] no skeletal isomerization, i.e. formation of isobutene was detected. The amount of photo-formed products other than butene isomers was negligible, although small amounts of butenes were irreversibly adsorbed onto the catalysts.

The initial rates of the photoisomerization determined from the slopes of the plots of the amount reacted vs. reaction time are shown in Table 1, which includes the rates of the isomerization in the dark. It is clear that the isomerization in the dark is much slower than the photoisomerization. Furthermore, as shown in Fig. 1 after the UV irradiation ceased, no isomerization occurred. It is concluded, therefore, that the isomerization of 2-butene in the dark hardly takes place over TiO_2 at around 313 K, i. e., the observed photoisomerization of 2-butene is not associated with the thermal effect by UV irradiation. Thus, a much higher reactivity of 2-butene as compared with 1-butene shown in Table 1 has been established. Such features are completely different from those of the isomerization in the dark where 1-butene is more reactive than 2-butene.

2. Effect of the Addition of O_2 or NO Molecules upon the Photoisomerization. The addition of NO molecules leads to the complete inhibition of photoisomerization of *cis*-2-butene and *trans*-2-butene. Figure 3 shows the results for *trans*-2-butene. The inhibition was also observed in the dark isomerization of 1-butene. Lunsford et al.[7] have found that the addition of NO molecules leads to the inhibition of the dark isomerization of butene over Al_2O_3. Lunsford et al.[8] and Che et al.[9] showed that on the surface of Al_2O_3 and TiO_2 the paramagnetic NO molecules interact with exposed Al and Ti ions, respectively, by using ESR.

A similar inhibition of photoisomerization of *cis*-2-butene as well as of *trans*-2-butene was observed with the addition of oxygen. In this case the photooxidation reactions took place in place of photoisomerization. Details of the photooxidation of alkenes such as butenes have been reported elsewhere.[10]

3. ESR Measurements of the Catalysts. In connection with the inhibition of the photocatalytic isomerization caused by added O_2 or NO, ESR measurements have been carried out. The addition of O_2 onto the TiO_2 catalyst degassed at high temperature leads to the formation of O_2^- anion radicals having *g*-values, $g_1=g_{zz}=2.020$, $g_2=g_{yy}=2.0106$, and $g_3=g_{xx}=2.0046$, being in good agreement with those given in many literatures.[11] This species is very stable

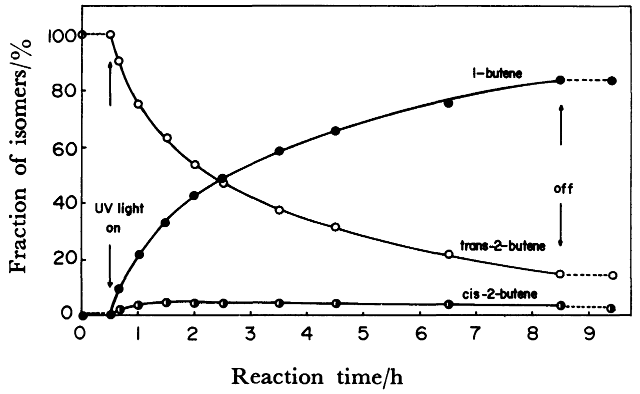

Fig. 1. Photocatalytic isomerization of *trans*-2-butene over TiO_2 catalyst at 313 K. Amount of used TiO_2 (P-25) is 0.3 g. Initial pressure of *trans*-2-butene is 4.0 kPa (30 Torr).

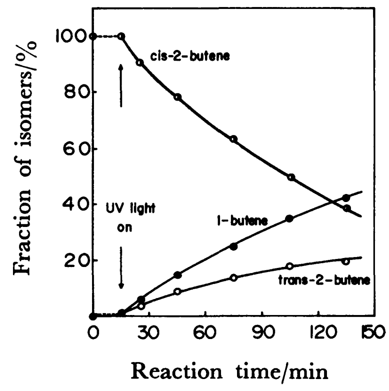

Fig. 2. Photocatalytic isomerization of *cis*-2-butene over TiO_2 catalyst at 313 K. Amount of used TiO_2 (P-25) is 0.3 g. Initial pressure of *cis*-2-butene is 4.0 kPa (30 Torr).

Table 1. Rates of Isomerization of Butenes over TiO_2 at 313 K

Catalyst	Condition	Temperature	Initial rate/10^{-9} mol s^{-1}					
		K	*cis*→*trans*	*cis*→1	*trans*→*cis*	*trans*→1	1→*cis*	1→*trans*
TiO_2 (P-25)[a]	Under UV	313	15.3	16.9	4.12	13.5	2.61	0.68
TiO_2 (rutile)[b]	Under UV	313	5.46	18.2	3.92	9.00	0.64	0.09
TiO_2 (P-25)[a]	Dark	313	0.127	0.122	0.065	0.063	2.60	0.65

Initial pressure of butenes: 4.0 kPa (30 Torr). a) Amount of used TiO_2=0.3 g, b) Amount of used TiO_2=0.6 g.

even at higher temperature (up to around 373 K). Figure 4 shows the new ESR signal which appears by UV irradiation of TiO_2 at 77 K in the presence of O_2. This new signal is obtained as a differential spectrum by subtracting the spectrum of before UV irradiation from the spectrum of after UV irradiation at 77 K. This new ESR signal having g_1=2.0080 and g_2=2.0015 could be assigned to the O_3^- anion radicals, since the shape and paramagnetic parameters of the spectrum are in good agreement with those for the O_3^- anion radicals on TiO_2.[12] This suggests that the following reaction occurs on the TiO_2 under UV irradiation.

$$O^- + O_2 \rightarrow O_3^-,$$

where O^- is the photo-formed hole center. Details of the photo-formed O_3^- have been described in the previous papers.[10,13]

Figure 5 shows the ESR spectrum of the NO molecules adsorbed onto TiO_2 degassed at high temperature. As reported by a number of workers,[8–10] NO molecules adsorbed onto the solid surface shows the ESR spectrum due to partially quenching of the spin-orbit coupling. The ESR spectrum characterized by g_1=2.003 and g_2=1.920 is assigned to NO radicals coordinated with exposed Ti^{4+} ions on the surfaces.[9] This radical species can be easily removed from the surface by degassing the catalyst at around 300 K, being in agreement with previous works.[8,9,14] The high concentration of NO molecules on the surface results in the rather poorly resolved spectrum. On UV irradiation of the TiO_2 containing NO essentially no change was observed with the signal due to the radicals. Recently, Pichat et al.[15] have reported that NO molecules photodecompose over TiO_2 through the interaction with the O^- hole center as follows:

$$O^- + NO_{ad}^- \longrightarrow N_{ad} + O_{ad} + O^{2-}.$$

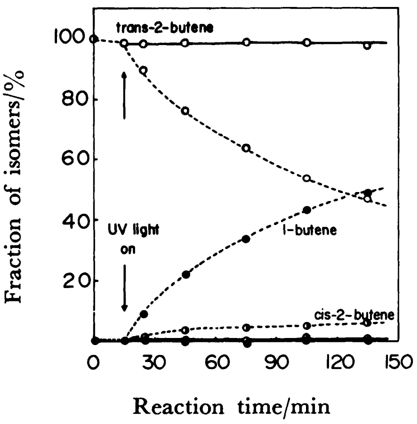

Fig. 3. Effect of the addition of NO molecules upon the photocatalytic isomerization of *trans*-2-butene over TiO_2 catalyst at 313 K. Amount of used TiO_2 (P-25) is 0.3 g. Pressures of *trans*-2-butene and NO molecule are 4.0 and 0.67 kPa, respectively. Solid lines: in the presence of NO molecules; dotted lines: in the absence of NO molecules.

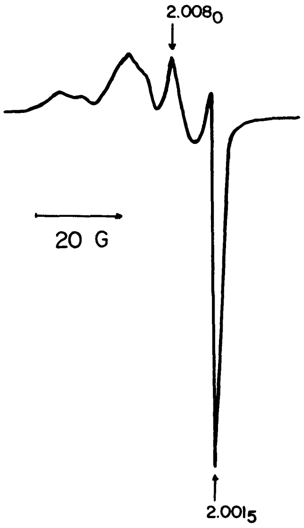

Fig. 4. ESR spectrum of photo-formed O_3^- anion radicals on TiO_2 catalyst at 77 K. Initial pressure of O_2 onto TiO_2 (rutile) is 0.33 kPa (2.5 Torr). UV irradiation was carried out at 77 K by using 500 W Hg lamp (λ>280 nm). Amount of photo-formed O_3^- anion radicals: 2×10^{-6} mol/g.

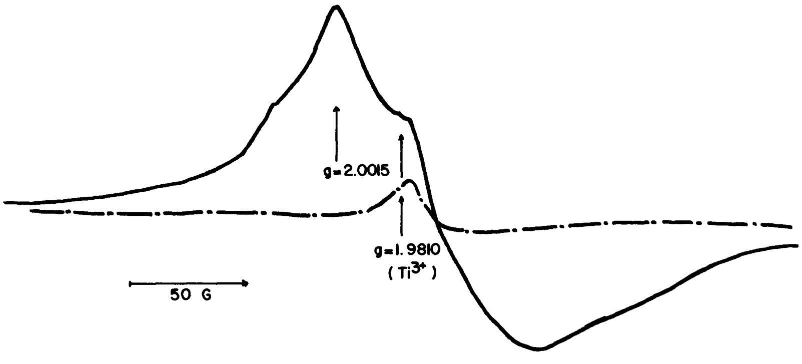

Fig. 5. ESR spectrum of adsorbed NO molecules on TiO_2 catalyst at 77 K. ESR spectra were recorded at 77 K. Amount of adsorbed NO: 2.1×10^{-5} mol/g.

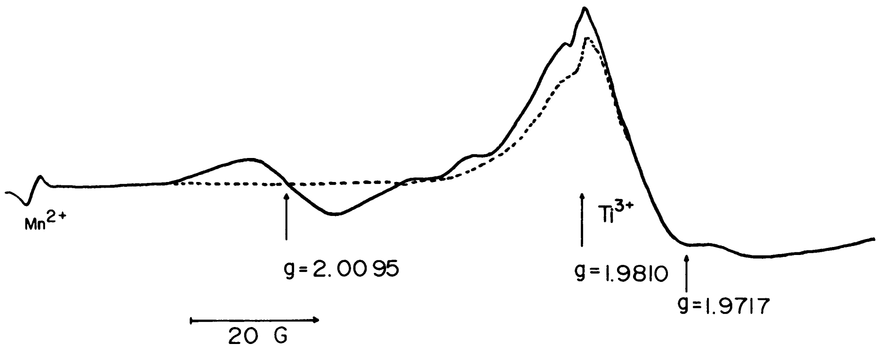

Fig. 6. ESR spectrum obtained before and after UV irradiation of TiO_2 catalyst at 77 K in the presence of adsorbed 1-butene. ESR spectra were recorded at 77 K. UV irradiation was carried out at 77 K for 30 min. Amount of adsorbed 1-butene: 1.1×10^{-5} mol/g. Dotted line: before UV irradiation; solid line: under UV irradiation.

Furthermore, as described in the previous paper,[6] the interaction of NO with photo-formed O^- species has been established. From the above considerations the following conclusions emerge: UV irradiation of TiO_2 results in formation of O^- or $[Ti^{3+}-O^-]$ pairs, although the O^- species is not detected directly by ESR, probably because of its short lifetime even at 77 K and/or incomplete removal of the degeneracy of the p-orbitals in this species, as suggested by Kazansky;[16] the O^- species thus formed interacts with NO or O_2 molecules in a manner similar with ZnO. Thus, the inhibition of the photocatalytic isomerization by added NO and O_2 is explicable.

The TiO_2 sample degassed at 833 K exhibited the ESR signal due to the Ti^{3+} ions and the O^- ions in the bulk at 77 K. The addition of butene molecules onto the catalyst at 300 K induced a slight increase in the signal due to the Ti^{3+} ions. This suggests that some fraction of Ti^{3+} ions interact with butene molecules. As shown in Fig. 6, the UV irradiation of TiO_2 in the presence of butenes at 77 K leads to the increase in the Ti^{3+} signal with UV irradiation time. Simultaneously, a broad signal with $g=2.0095$ appears. This signal is very unstable, and disappeared completely on raising the catalyst temperature to about 180 K. Although it is not possible to assign the species, the increase in the Ti^{3+} ion signal suggests that this unstable species might be formed through the reaction of butene with photo-formed O^- hole center. The occurrence of the photoreaction is in good agreement with the results obtained by Volodin et al.[17] who investigated the photoreduction of TiO_2 in the temperature range or 90—400 K. As shown in the preceding paper,[6] formation of a radical species has been demonstrated clearly by ESR under UV irradiation of ZnO in the presence of 1-butene at 77 K. The poorly resolved ESR spectrum may arise from the high concentration of butene adsorbed on the surface at 77 K and/or mixing of several type of radical species.

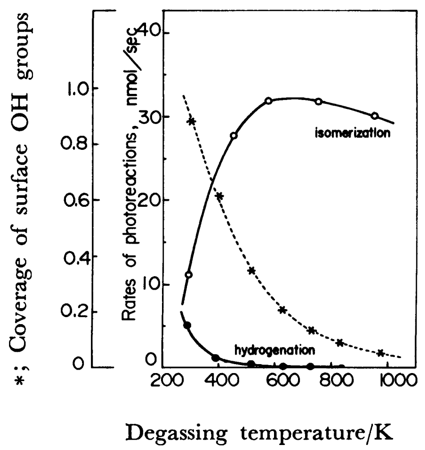

Fig. 7. Effect of the adsorbed H_2O upon the photocatalytic isomerization of *cis*-2-butene and the photocatalytic hydrogenation of $CH_3-C\equiv CH$ over TiO_2 catalyst at 313 K. H_2O vapor was adsorbed at 313 K until a pressure of 1.3 kPa (10 Torr) was reached, after which the degassing of the catalyst was carried out at each temperatures for 30 min. Initial pressure of *cis*-2-butene or $CH_3-C\equiv CH$ is 4.0 kPa (30 Torr). Coverage of H_2O was difined as ([amount of adsorbed H_2O]-[amount of desorbed H_2O])/[amount of adsorbed H_2O]. Amount of used TiO_2 (P-25): 0.3 g.

4. Effect of Remaining Water Adsorbed on the Photocatalytic Isomerization. The effect of the adsorbed water on the photocatalytic isomerization has been investigated in order to obtain further information on the active sites for the reaction. As shown in Fig. 7, the rates of photoisomerization reaction increases, passing through a maximum and then decreases. While, the increase in the degassing temperature results in the decrease in the yields of photohydrogenation of $CH_3-C\equiv CH$ (or *cis*-2-butene) where simultaneous activation of alkyne (or alkene) and H_2O is involved.[18]

When photo-formed O^- species plays a significant role in the photocatalytic isomerization, its rate is expected to increase with increasing the degassing temperature, since the concentration of the presence of O^- species (i.e. O^{2-} ions) becomes larger. The presence of a maximum rate suggests that the surface OH^- groups is involved in the photocatalytic isomerization. From the results in Fig. 7, it is clear that on the surface of TiO_2 containing water (wet surfaces) UV irradiation leads to the photohydrogenation reactions, where simultaneous activation of alkyne (or alkene) and H_2O is involved, while on the surfaces of TiO_2 (dry surfaces) the double bond shift isomerization (1,3-hydrogen shift) occurs with high efficiency.

In order to obtain information on the role of surface OH^- groups in the photocatalytic isomerization reactions, the photoisomerization reactions of *cis*-2-butene have been undertaken over TiO_2 catalysts, which was subjected to pretreatment with D_2O followed by evacuation at 773 K. As shown in Fig. 8, deuterium substitution has no effect on the rates of double bond shift isomerization as well as cis-trans isomerization reactions. Table 2 shows the results of the distribution of D-atom in the photo-formed products and the reactant. It is clear that D-atom is incorporated into the photo-formed 1-butene, though its extent is not high. On the other hand, within the experimental error no D-atom incorporation is observed with *cis*- and *trans*-2-butene. Thus, participation of surface OH^- species in the photocatalytic isomerization is confirmed.

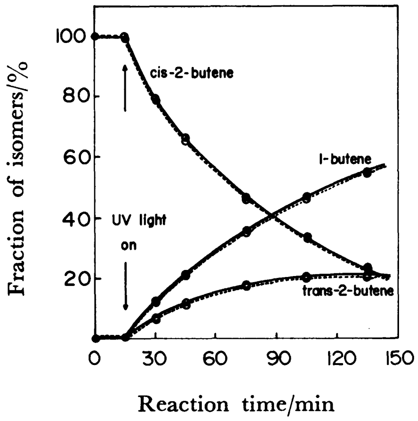

Fig. 8. Effect of the D_2O pretreatment of TiO_2 catalyst upon the photocatalytic isomerization of *cis*-2-butene over TiO_2 at 313 K. D_2O vapor was introduced onto the catalyst, kept for enough time, and then degassed at 453 K. This treatment was repeated several times. Solid lines: treated with H_2O; dotted lines: treated with D_2O. Amount of used TiO_2 (P-25): 0.3 g.

5. Mechanism for the Photocatalytic Isomerization of Butene. It has been reported by many workers that with TiO_2 catalysts degassed at higher temperatures (at around 900 K), the isomerization of butene proceeds via π-allyl carbanion intermediates.[19] In this mechanism the key step is abstraction of hydrogen from butene molecules, which is easier with 1-butene than with 2-butene. Such feature has been established as the characteristic of the dark isomerization. As described above, in the photocatalytic isomerization of butenes the reactivity of 2-butene is much higher than that of 1-butene, product distribution being completely different from that predicted from thermodynamic equilibrium. These clearly indicate not only that the photocatalytic isomerization reaction is kinetically controlled, as described in the previous paper,[6] but also that the active species associated with the photocatalytic isomerization is quite different from that in the dark isomerization reactions. The results of the ESR and inhibition studies described above clearly demonstrate that the interaction of photo-formed O^- species or $[Ti^{3+}\text{-}O^-]$ pair with butene molecules is involved in its photocatalytic isomerization.

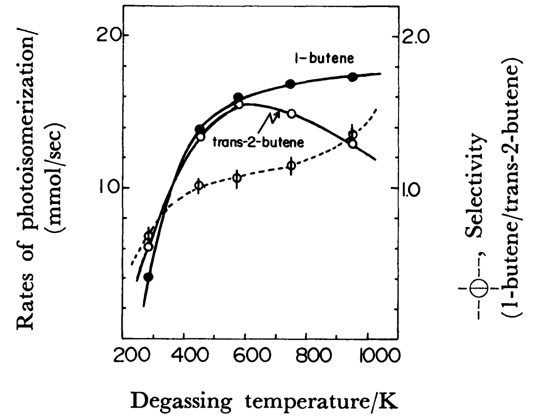

Fig. 9. Effect of the adsorbed H_2O upon the rate of photocatalytic isomerization and the selectivity of isomerization over TiO_2 at 313 K. Experimental condition is same to Fig. 7.

Table 2. Distribution of D-Atom in the Products Formed from the Photocatalytic Isomerization of *cis*-2-Butene over TiO_2 at 313 K

	Before photoreaction/%	After photoreaction/%		
	cis-2-butene	*cis*-2-butene	1-butene	*trans*-2-butene
$m/e^- = 56$	96.11	92.46	84.94	93.12
$m/e^- = 57$	3.89	7.54	15.06	6.88
Conversion of exchange (%)		3.65	11.17	2.99

D_2O vapor was adsorbed at 313 K until a pressure of 1.3 kPa (10 Torr) was reached, after which the evacuation was carried out at 453 K.

Recently, we have reported that the charge transfer excited states, complex, $[Mo^{5+}-O^{-}]^*$, of supported MoO_3 catalyst easily react with alkenes resulting in the fission of C=C bond of alkene molecule.[4b,20] It is likely, therefore, the closely existent electron and hole state, $[Ti^{3+}-O^{-}]$, of TiO_2 reacts with butene molecule to produce a corresponding radical species resulting from the opening of the C=C bond of butene in a manner similar to that with MoO_3 catalyst. As shown in Fig. 6, the ESR studies suggest that the photo-formed O^- species interacts with a butene molecule to form a radical species, though the spectrum is not well resolved due to high concentration of adsorbed butene.

Accordingly, it might be concluded that the photocatalytic isomerization of butene over TiO_2 proceeds according to a mechanism similar to that proposed for ZnO in the preceding paper:[6] Butene interacts with photo-formed O^- species to form a radical species. When this reverts to butene, the cis-trans isomerization will occur. The presence of H atom appears to be prerequisite for the occurrence of the double bond migration. Consequently, the more acidic the surface OH^- groups as well as the larger concentration of electron available for the neutralization of protons, the more efficient double bond migration results. As shown in Fig. 9, with increasing degassing temperature of TiO_2, the reactivity towards 1-butene formation monotonously increases. This suggests that supply of protons, i.e. the acidity of surface OH^- groups is not important in bringing about double bond migration. Accordingly, the increase in the selectivity towards 1-butene formation may be attributed to the increase in the concentration of electrons available for the neutralization of protons. Further study is necessary to clarify the nature of such an increase in the selectivity towards 1-butene formation.

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