Photocatalytic Isomerization of Butenes over ZnO and SnO_2

Sukeya Kodama,* Masaaki Yabuta, Masakazu Anpo, and Yutaka Kubokawa
Department of Applied Chemistry, University of Osaka Prefecture, Sakai, Osaka 591

(Received April 1, 1985)

It has been found with ZnO as well as TiO_2 that 2-butene is much more reactive than 1-butene for their photocatalytic isomerization. Although both *cis-trans* and double bond isomerizations take place on ZnO, only *cis-trans* isomerization occurs over SnO_2. The photocatalytic isomerizations were suppressed drastically in the presence of NO. From those results together with the ESR studies the following conclusions emerge: a butene molecule interacts with the photoformed O^- to form a radical species as a result of fission of the C=C bond; the photocatalytic isomerization proceeds *via* such a radical intermediate; the lack of the reactivity of 1-butene appears to be explicable on such basis.

In order to understand the photocatalysis of metal oxides, it seems necessary to investigate on a wide range of the photocatalytic reactions, other than the oxidation and reduction reactions. From such standpoint we have investigated the photocatalytic isomerization of butenes over TiO_2 and ZnO with the result that in the case of TiO_2 2-butene is more reactive than 1-butene.[1] A continued study concerning the isomerization over ZnO has revealed that it is unnecessary to propose an intermediate different from that for the isomerization over TiO_2. Essentially the same features have been observed with both ZnO and TiO_2. Similar works have been extended to SnO_2.[2] In addition to those results, the present paper deals with the ESR studies which provide information on the active species as well as an intermediate in the photocatalytic isomerization of butenes. Furthermore, its mechanism has been worked out.

Experimental

All the butenes used in the present work as well as NO were of extrapure grade from the Takachiho Kagakukogyo Co. ZnO (Kadox 25, 10 $m^2 g^{-1}$) was obtained from New Jersey Zinc Co. SnO_2 (8.6 $m^2 g^{-1}$) was prepared from hydrolysis of $SnCl_2$ with aqueous ammonia. Both ZnO and SnO_2 were subjected to oxygen treatment for one hour at 560 °C followed by evacuation at the same temperature. Butenes of about 4.0 kPa were introduced over the catalysts (ZnO 0.6 g, SnO_2 2.0 g) which had been spread on the quartz cell window, having a surface area of *ca.* 32 cm^2. The photoisomerization was carried out by UV irradiation from a high pressure mercury lamp (Toshiba, SHL-100UV) with and without a filter (Toshiba, UV-D33S) shading the visible and infrared regions. Gas samples were taken at definite intervals and analyzed gas chromatographically using a dimethylsulfolane column. ESR measurements were carried out with JES-ME-1 (X-band). Mn^{2+} ions in MgO powder were used for g value and sweep calibration.

Results

Continued work concerning the isomerization of 1-butene over ZnO at 0 °C was carried out in the dark and under UV irradiation with and without the filter with the results shown in Fig. 1. No enhancement of the isomerization by UV irradiation was found. Figure 2 shows the results on the isomerization of *trans*-2-butene over ZnO at 0 °C. It is found that both isomerizations to *cis*-2-butene and 1-butene are enhanced by UV irradiation. From those results the following conclusions emerge: the enhancement of the isomerizations of 2-butene under UV irradiation arises from photocatalytic effects and not thermal effects by the radiation from the lamp; 1-butene is unreactive for

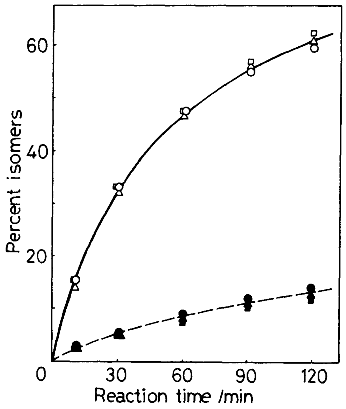


Fig. 1. Isomerization of 1-butene over ZnO at 0 °C. Solid curve: *cis*-2-butene; broken curve: *trans*-2-butene.
○, ●: Under UV without filter; △, ▲: under UV with filter; □, ■: in the dark.

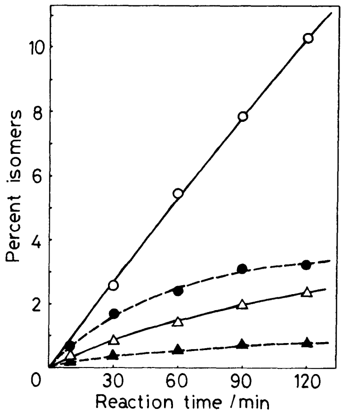


Fig. 2. Isomerization of *trans*-2-butene over ZnO at 0 °C.
Solid curve: under UV with filter; broken curve: in the dark. ○, ●: *cis*-2-Butene; △, ▲: 1-butene.

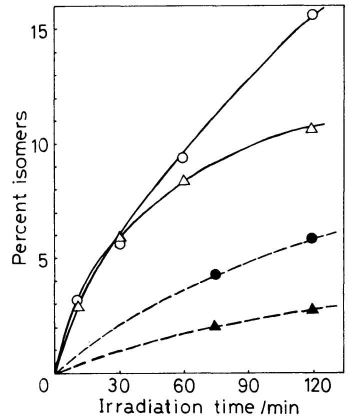


Fig. 3. Photoisomerization of *cis*-2-butene over ZnO at 0 °C.
Solid curve: without NO; broken curve: with NO of 1.3 kPa. ○, ●: *trans*-2-Butene; △, ▲: 1-butene.

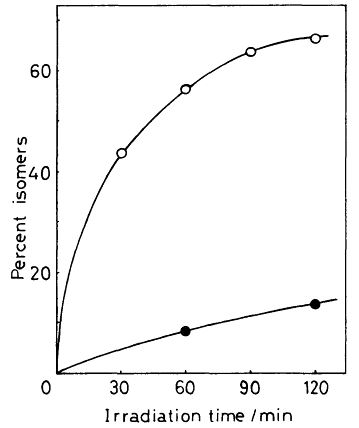


Fig. 4. Photoisomerization of *cis*-2-butene to *trans*-2-butene over SnO_2 at 40 °C. ○: Without NO; ●: with NO of 1.3 kPa.

photocatalytic isomerization. Thus, the conclusion obtained with TiO_2 that 2-butene is much more reactive than 1-butene holds for ZnO. Its general applicability is confirmed. As shown in Fig. 3, the photocatalytic isomerization of *cis*-2-butene is suppressed by the presence of NO.

Similar studies have been extended to SnO_2. The results are shown in Fig. 4. It should be noted that only *cis-trans* isomerization proceeds, without double bond migration. The isomerization is again restrained in the presence of NO.

When NO molecules were adsorbed onto the catalyst, which had been treated in vacuum, the ESR spectrum due to the adsorbed NO molecules was observed at 77 K.[3] UV irradiation of the catalyst in the presence of NO at 77 K led to the appearance of a new signal shown in Fig. 5, which was thermally unstable and it disappeared completely on raising the temperature up to 300 K. This new spectrum is characterized by g value of 2.002 with hyperfine splitting of *ca.* 35 G† for N^{14}.

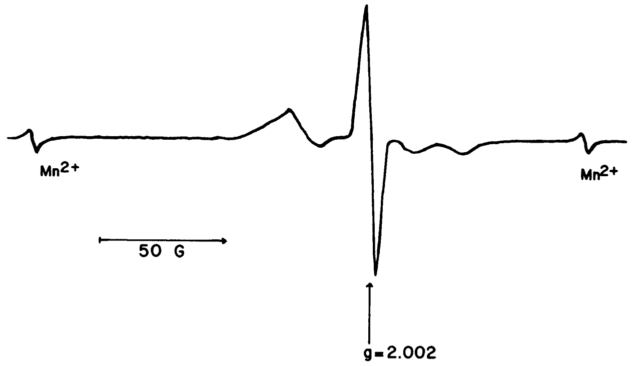


Fig. 5. ESR spectrum of photoformed NO_2^{2-} anion radicals adsorbed on ZnO (0.20 g) at 77 K. Amount of photoformed NO_2^{2-} is 8.6×10^{-7} mol.

These values are similar to those for NO_2^{2-} species adsorbed on the surface of ZnO, though the hyperfine splitting of 35 G is slightly smaller.[3b)] As described previously,[4)] UV irradiation of ZnO at 77 K *in vacuo* leads the formation of O^- anion radicals. Accordingly, it is expected that the photoformed O^- species reacts with NO to produce NO_2^-, which is transformed to NO_2^{2-} by electron trapping. This assumption is strongly supported from the results of ESR measurements. From these results, it is concluded that the spectrum shown in Fig. 5 can be assigned to NO_2^{2-}. Thus, the reaction of photoformed O^- with NO is confirmed. Since the photocatalytic isomerization is suppressed by the presence of NO as described above, it is suggested that interaction of butene molecules with photoformed O^- is involved in its photocatalytic isomerization.

The catalyst exhibited the ESR spectrum due to the presence of Zn^+ and bulk O^- species after the pretreatment in vacuum.[5)] When 1-butene was admitted onto the catalyst, a new ESR spectrum was observed neither at 77 K nor at room temperature, except for a slight weakening of the signal due to O^- species. On UV irradiation of the catalyst in the presence of butene at 77 K, a new ESR signal appears as shown in Fig. 6. It shows a doublet hyperfine splitting separated by *ca.* 22 G. This splitting is comparable to the 17—22 G splitting due to one *β*-hydrogen in alkyl or alkene radicals.[6)] Further triplet hyperfine splitting with *ca.* 7 G is similar to that for two *α*-hydrogens in alkene cation radicals adsorbed on zeolite surfaces.[7)] When the temperature was raised up to around 300 K, this signal disappeared irreversibly without appearance of any new signals. In addition to such hyperfine splitting, the number of hyperfine components, *i.e.*, a doublet of triplet and their intensity ratio together with a g value of 2.0014 suggest that a radical species, $CH_2\dot{-}CH-CH_2-CH_3$, is formed on ZnO under UV irradiation.

Discussion

The fact that 2-butene is much more reactive than

---

† $1\ G \approx 10^{-4}\ T$.

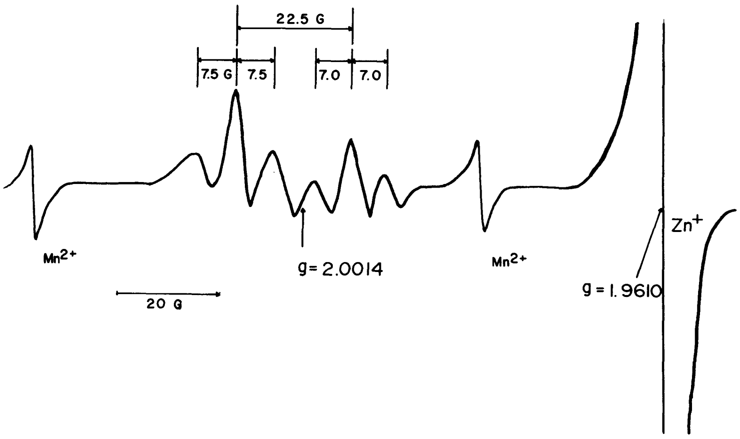
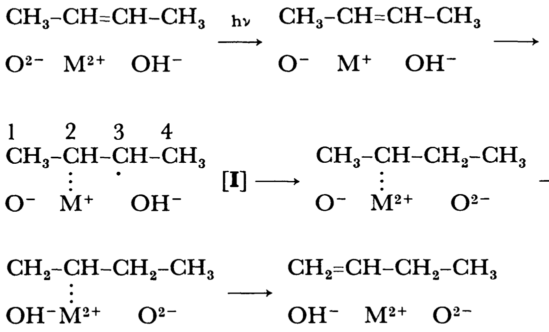


Fig. 6. ESR spectrum of photoformed butene radicals at 77 K. Amount of 1-butene adsorbed on ZnO (0.20 g) is 1.2×10^{-5} mol g^{-1}.

1-butene is unexplicable by π-allyl intermediates, which has been proposed for the isomerization of butenes over ZnO and Al_2O_3.[8] This suggests that an intermediate different from π-allyl species is involved in the photocatalytic isomerization. In the previous works[9] it has been shown that fission of the C=C bond of alkenes is induced by its interaction of photoformed O^- or $[M^{(n-1)+}—O^-]$ pairs. Furthermore, the ESR studies described above demonstrate clearly that the photoformed O^- species interacts with a butene molecule to form a radical species. Accordingly, it might be concluded that a radical species is involved as the intermediate in the photocatalytic isomerization. Thus, the following reaction scheme is proposed for the 2-butene isomerization:

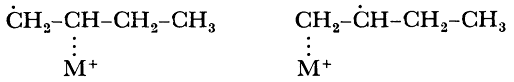


$$\begin{array}{ccc} \begin{array}{c} CH_3\text{-}CH{=}CH\text{-}CH_3 \\ O^{2-}\ \ M^{2+}\ \ OH^- \end{array} & \xrightarrow{h\nu} & \begin{array}{c} CH_3\text{-}CH{=}CH\text{-}CH_3 \\ O^-\ \ M^+\ \ OH^- \end{array} \longrightarrow \\ \begin{array}{c} 1\quad 2\quad 3\quad 4 \\ CH_3\text{-}CH\text{-}\dot{C}H\text{-}CH_3 \\ \vdots \\ O^-\ \ M^+\ \ OH^- \end{array} & [\mathbf{I}] \longrightarrow & \begin{array}{c} CH_3\text{-}CH\text{-}CH_2\text{-}CH_3 \\ \vdots \\ O^-\ \ M^{2+}\ \ O^{2-} \end{array} \longrightarrow \\ \begin{array}{c} CH_2\text{-}CH\text{-}CH_2\text{-}CH_3 \\ \vdots \\ OH^-M^{2+}\ \ O^{2-} \end{array} & \longrightarrow & \begin{array}{c} CH_2{=}CH\text{-}CH_2\text{-}CH_3 \\ OH^-\ \ M^{2+}\ \ O^{2-} \end{array} \end{array}$$

The photoformed O^- or $[M^{(n-1)+}—O^-]$ pairs interact with a butene molecule to form the radical [**I**] as a result of opening of the C=C bond. When the radical reverts to butene, the *cis-trans* isomerization is expected to occur. In fact, Morikawa *et al.*[10] have proposed that such radical species adsorbed on porous Vycor glass play a significant role in the photocatalytic *cis-trans* isomerization of butenes on it.

In case where the double bond migration proceeds *via* a radical intermediate, the presence of hydrogen atoms appears to be the prerequisite for its occurrence. If H atoms are present on the surface, H atom addition to C atom at the position 3 of the radical [I] will occur. This will be followed by removal of H atom from CH_3 group by the O^- species because of its high efficiency for hydrogen abstraction. Thus, 1-butene is formed. In the above reaction scheme it is assumed that H atoms are supplied from the surface OH groups, although there is no evidence for this postulate. In this case the acidity of the OH groups as well as the concentration of electrons available for the neutralization of protons would determine to what extent the double bond migration occurs. The photoformed electrons trapped as M^+ ions are used for the neutralization of protons. At present it is unclear whether or not the difference in the selectivity of the isomerization between ZnO and SnO_2 described above is explicable on the basis of such a concept. A further study is necessary to settle this problem. It is to be noted that trace amounts of the OH groups are enough to bring about the isomerization in the case of a concerted mechanism where the removal and addition of H atom proceed with a similar rate.

In the case of the isomerization of 1-butene, in contrast to the case of 2-butene where opening of the C=C bond brings about only one type of the adsorbed radical, two types of the adsorbed radicals may be expected to be formed:



$$\begin{array}{cc} \begin{array}{c} \dot{C}H_2\text{-}CH\text{-}CH_2\text{-}CH_3 \\ \vdots \\ M^+ \end{array} & \begin{array}{c} CH_2\text{-}\dot{C}H\text{-}CH_2\text{-}CH_3 \\ \vdots \\ M^+ \end{array} \end{array}$$

(primary radical) (secondary radical)

Although for the primary radical the removal and addition of H atom may be possible, for the secondary radical only regeneration of 1-butene may take place. Since it is well-known that the secondary radical is more stable than the primary one, the secondary radical is expected to participate in the reaction. Accordingly, in the case of 1-butene occurrence of the isomerization is not expected, in agreement with the experimental results. Finally it should be noted that the unusual feature of the photocatalytic isomerization, *i.e.*, the lack of the reactivity of 1-butene is explicable on the basis of the concept that an intermediate where one unpaired electron remains uninteracted with the surface is involved in the reaction.

References

1) S. Kodama, M. Yabuta, and Y. Kubokawa, *Chem. Lett.*, **1982**, 1671.

2) C. Kemball, H. F. Leach, and I. R. Shannon, *J. Catal.*, **29**, 99 (1973); M. Itoh, H. Hattori, and K. Tanabe, *ibid.*, **43**, 192 (1976); J. Herrmann, J. Disdler, and P. Pichat, *J. Chem. Soc., Faraday Trans. 1*, **77**, 2815 (1981).

3) a) J. H. Lunsford, *J. Chem. Phys.*, **46**, 4347 (1967); b) J. H. Lunsford, *J. Phys. Chem.*, **72**, 2141 (1968); c) J. H. Lunsford, *ibid.*, **72**, 4163 (1968).

4) M. Anpo and Y. Kubokawa, *J. Phys. Chem.*, **88**, 5556 (1984).

5) K. M. Sancier, *J. Catal.*, **5**, 314 (1966); J. H. C. Van Hooff, *ibid.*, **11**, 277 (1968).

6) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); J. E. Wertz and J. R. Bolton, "Electron Spin Resonance Elementary Theory and Practical Applications," McGraw-Hill Book Co., New York (1972).

7) S. Shin, *J. Catal.*, **36**, 238 (1975).

8) C. C. Chang, W. C. Conner, and R. J. Kokes, *J. Phys. Chem.*, **77**, 1957 (1973); J. H. Lunsford, L. W. Zingery, and M. P. Rosynek, *J. Catal.*, **38**, 179 (1975).

9) M. Anpo, I. Tanahashi, and Y. Kubokawa, *J. Chem. Soc., Faraday Trans. 1*, **78**, 2121 (1982); M. Anpo, N. Aikawa, S. Kodama, and Y. Kubokawa, *J. Phys. Chem.*, **88**, 2569 (1984).

10) A. Morikawa, M. Hattori, K. Yagi, and K. Otsuka, *Z. Phys. Chem. (Frankfurt am Main)*, **104**, 309 (1977).