

PHOTOCATALYTIC ISOMERIZATION OF BUTENES OVER TiO_2 AND ZnO

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Photocatalytic isomerization of butenes over ZnO and TiO_2 has been investigated. With ZnO , 1-butene is more reactive than 2-butene, photoenhancement in the isomerization being attributable to photoformed O^- hole centers. With TiO_2 , 2-butene is more reactive than 1-butene, which would result from a stronger interaction of the C=C bond of 2-butene with UV irradiated TiO_2 .

Photocatalysis of metal oxides has recently received much attention from the standpoint of utilization of solar energy. Information on the reactivity of the active species formed by trapping electrons or holes such as O^- species is important for the understanding of the photocatalysis. In order to obtain such information it seems necessary to investigate the photocatalytic effect with a wide range of the catalytic reactions, other than the oxidation and reduction reactions. Accordingly, it has been undertaken to investigate the photocatalytic isomerization of butenes over TiO_2 and ZnO , since the mechanism as well as the intermediates of the isomerization in the dark has been extensively studied by a number of workers.¹⁾

A closed circulation system was used. Butenes were introduced to the TiO_2 , P-25 (Degussa; 40 m^2/g , its major component is anatase) and the ZnO , Kadox 25 (New Jersey Zinc Co.; 10 m^2/g) which had been subjected to oxygen treatment at 560°C followed by evacuation at the same temperature. The pressure of butenes was about 4.0 kPa. UV irradiation was carried out by a high pressure mercury lamp without a filter. Gas samples were taken at definite intervals and analyzed gas chromatographically. The rate of isomerization was determined from the initial slopes of the plots of the amount reacted vs. time.

Figure 1 shows the results obtained with trans-2-butene - TiO_2 system. No skeletal isomerization occurred. The formation of the products other than butene isomers was

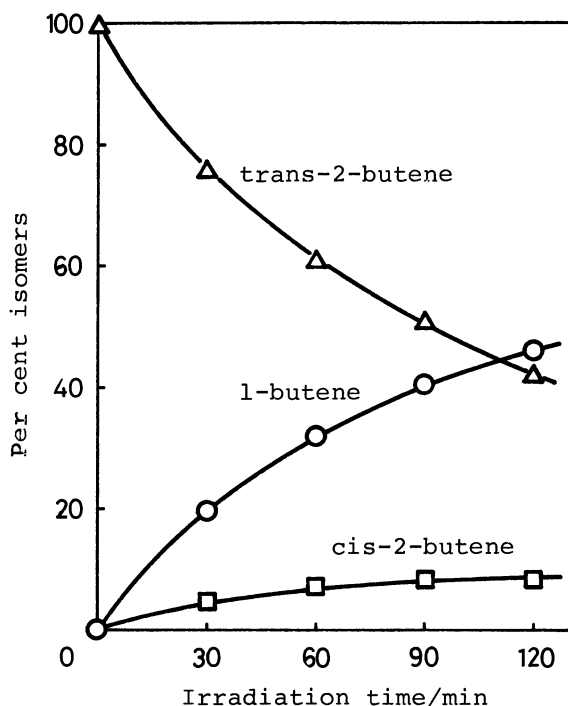


Figure 1. Photoisomerization of trans-2-butene over TiO_2 .

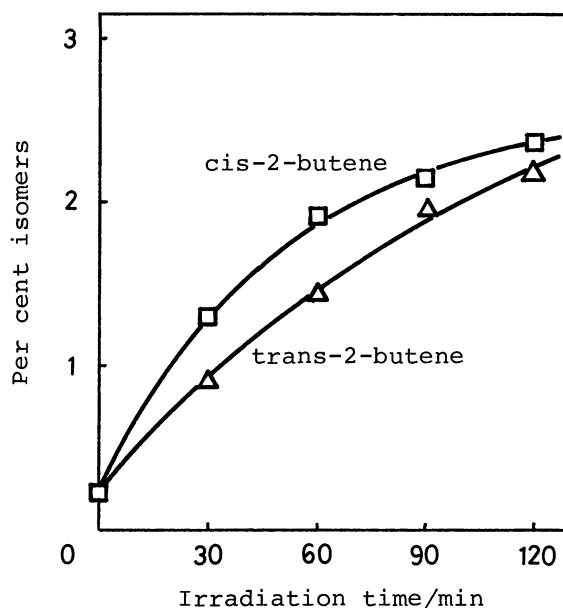


Figure 2. Photoisomerization of 1-butene over TiO_2 .

negligible although some part of trans-2-butene was irreversibly adsorbed under UV irradiation. After irradiation ceased, no isomerization occurred. Similar behaviors were also observed with other butenes. The isomerization in the dark hardly took place around 40°C which is the temperature of the UV irradiated TiO_2 . This suggests

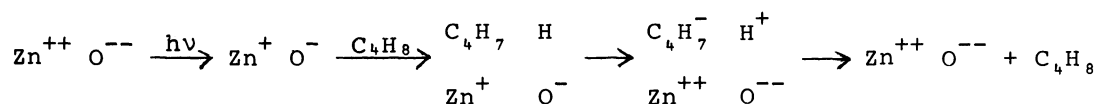
Table. Rates of isomerization^{a)}

Catalyst ^{b)}	Temp. ($^\circ\text{C}$)	Initial rate (n mol/s)					
		cis \rightarrow trans	cis \rightarrow 1	trans \rightarrow cis	trans \rightarrow 1	1 \rightarrow cis	1 \rightarrow trans
TiO_2 (under UV) ^{c)}	40	15.3	16.9	4.12	13.5	0.98	0.49
TiO_2 (in dark)	100	0.22	0.42	0.33	0.39	21.6	1.71
ZnO (under UV)	0 ^{d)}	0.58	2.76	1.41	0.41	9.86	1.40
ZnO (in dark)	0	0.90	0.95	0.44	0.19	4.66	0.82

a) Comparison of the photocatalytic activity between TiO_2 and ZnO seems very difficult owing to the difference in the extent of the surface layers activated by UV irradiation between both oxides. b) The catalyst weight is 300 mg for TiO_2 and 600 mg for ZnO. c) Similar rates were obtained with the TiO_2 reduced by hydrogen at 660°C . d) An ice cooled reactor removes the possibility of the temperature rise caused by UV irradiation.

that the observed photoisomerization is not associated with the thermal effect by UV irradiation. As shown in Fig. 2, the reactivity toward isomerization of 1-butene is markedly lower than that for trans-2-butene.

In the case of ZnO, the isomerization in the dark proceeded even at 0°C. Under UV irradiation the isomerization was enhanced as shown in Fig. 3. The rate of photoisomerization for ZnO was obtained from subtraction of the rate of isomerization in the dark. The rates thus obtained together with those for TiO₂ are shown in Table. There is no marked difference in the selectivities and reactivities observed for three butenes between the photoisomerization and the isomerization in the dark, suggesting that similar intermediates are involved in both isomerizations. Enhancement of the isomerization by UV irradiation appears to be attributable to photoformed O⁻ hole centers which exhibit a high reactivity for hydrogen abstraction.²⁾ The photocatalytic isomerization may be represented as follows:



where photoformed electrons as well as holes participate in the isomerization. Accordingly, the reactions catalyzed by Lewis acid and basic sites are induced by UV irradiation.

It should be noted that in the photoisomerization over TiO₂ 2-butene is more reactive than 1-butene, being in contrast to the features of the isomerization in the dark where the reverse situation is observed as has been shown by the studies on the butene isomerization on the oxides such as ZnO and Al₂O₃.¹⁾ Such a high reactivity of 1-butene is explained in terms of the concept that the isomerization proceeds via π -allyl intermediates, its key step being abstraction of hydrogen from butene molecules. In fact, in the isomerization in the dark over TiO₂ 1-butene is more reactive than

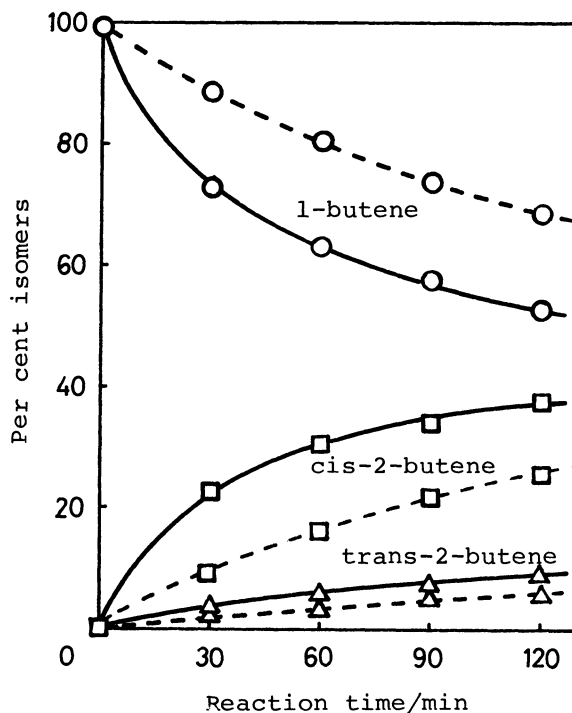


Figure 3. Photoisomerization (—) and isomerization in the dark (---) of 1-butene over ZnO.

2-butene (Table). Accordingly, it appears that an intermediate different from π -allyl species is involved in the photoisomerization over TiO_2 . In the previous work³⁾ it has been shown that the weakening of the C=C bond of alkenes is induced by its interaction with photoformed O^- hole centers or the charge-transfer excited states $[\text{Me}^{(n-1)+} - \text{O}^-]$. Morikawa and co-workers⁴⁾ have shown that UV irradiation of porous Vycor glass in the presence of cis-2-butene brings about the weakening of its C=C bond, which results in formation of trans-2-butene. This suggests that the interaction of the C=C bond of butene with irradiated TiO_2 play a significant role in its isomerization. A higher stability of the π -complex of 2-butene than that of 1-butene would result in a stronger interaction of the C=C bond of 2-butene⁵⁾ with irradiated TiO_2 . Thus, a higher reactivity toward photoisomerization of 2-butene appears to be explicable. Further work is necessary for elucidating the mechanism of the photoisomerization over TiO_2 .

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