The Catalytic Action of TiO_2 for the Isomerization of Butenes

Kunimitsu Morishige, Hideshi Hattori, and Kozo Tanabe

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

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The isomerization of 1-butene or *cis*-2-butene and the co-isomerization of *cis*-2-C_4H_8 and *cis*-2-C_4D_8 were carried out at 120 °C over TiO_2 calcined *in air*. It has been found that induction period appeared and the ratio of *cis*-2-butene to *trans*-2-butene in the isomerization of 1-butene was unusually high (5—20). The double bond migration and *cis-trans* isomerization occurred by an intramolecular hydrogen transfer reaction and the kinetic isotope effect (k_H/k_D) was 4—5. The activity was completely or almost lost by poisoning with pyridine or nitric oxide. The isomerization was concluded to proceed by a π-allyl anion mechanism, where the *cis-trans* interconversion is highly restricted and the C–H bond cleavage is involved in the rate-determining step of the double bond migration. Main active sites were suggested to consist of both Lewis acid sites and basic sites (surface oxygen ion, O^{2-}).

TiO_2 has been generally classified as a solid acid on the basis of the experiment on the chemical adsorption of basic Hammett indicators and pyridine.[1] Recently, however, Shannon *et al.* reported that TiO_2 calcined in air showed the similar selectivity as basic catalysts for the isomerization of *n*-butene.[2] From the experiment on co-isomerization of the mixture of C_4H_8 and C_4D_8, they concluded that both the double bond migration and *cis-trans* isomerization were mainly intermolecular and each isomerization proceeded *via* separate mechanisms. However, it seems to be difficult to determine whether the isomerizations are inter- or intra-molecular, since their results showed that considerable isotopic scrambling occurred independently of the isomerizations.

In our previous work, the nature of active sites on TiO_2 was found to depend strongly on the method of preparation and pretreatment of the catalyst.[3] Over TiO_2 prepared by calcining titanic acid *in vacuo* at low temperatures, the ratio of *cis*-2-butene/*trans*-2-butene (abbreviated as *cis-/trans-*) from 1-butene was nearly 1, indicating Brönsted acid as active sites. When TiO_2 was prepared by calcining titanic acid *in vacuo* at high temperatures, it gave the high *cis-/trans-* ratio. Since the activity of the latter catalyst was decreased by oxygen treatment, the active sites were concluded to be mainly Ti^{3+} ions formed by the reduction of Ti^{4+}. On the other hand, it was reported that the activity of TiO_2 calcined *in air* was not affected by oxygen treatment,[2] though no study was made on the nature of active sites.

The purpose of the present work is to elucidate the reaction mechanism as well as the nature of active sites for the isomerization of *n*-butene over TiO_2 prepared by calcining titanic acid *in air* and to learn about the relation of the acid sites on the catalyst with the basic character giving the high *cis-/trans-* ratio.

Experimental

Catalyst and Reagents. TiO_2 was prepared by hydrolyzing $TiCl_4$ with NH_4OH in the solution of $(NH_4)_2SO_4$ and calcining the precipitate in air at 500 °C for 3 hr. X-Ray diffraction of the sample showed a structure of an anatase type. Butenes (Takachiho pure grade) were purified by distilling through a molecular sieves 4A maintained at the temperature of dry ice–ethanol. Perdeuterio-*n*-butenes were prepared by exchange of 1-butene with D_2 over MgO at room temperature, the isomers being separated on a preparative scale chromatographic column.[4] Pyridine (GR of Kanto Chem. Co.) was purified by repeating three times the procedure of a freeze-thaw outgassing cycle after passing over zeolite 13X. NO of more than 95.0% purity supplied by the Gaschro Industry Co. was purified by a vacuum distillation.

Reaction Procedure. The isomerization of *n*-butenes was carried out in a circulating system of *ca.* 330 ml at 120 °C. A small amount (*ca.* 1%) of the reaction products was withdrawn out of the system by expansion at appropriate time intervals and analyzed by gas chromatography using a 7 m column (Cu tubing of 4 mm in diameter) containing 30% propylene carbonate on 30—60 mesh Uniport C. The column was operated at 0 °C. Before use, a catalyst (0.2 g) was treated in a vacuum of 10^{-4} mmHg at 450 °C for 2 hr. Between runs, the catalyst was degassed at 400 °C for 30 min. The same activity and selectivity as those of the first run were maintained by this simple treatment through all the kinetic runs. The surface area of the catalyst was 72 m^2/g.

For co-isomerization experiments, a mixture containing about equal amounts of light *cis*-2-butene (*cis*-C_4H_8) and heavy *cis*-2-butene (*cis*-C_4D_8) was co-isomerized on TiO_2 (18.9 mg) in a static system of 26 ml at 5 cmHg. The isomerized products were condensed into a liquid nitrogen trap, separated by preparative scale gas chromatography and analyzed for the isotopic composition by mass spectrometry. Four runs were carried out and each run was stopped at different conversions. The mixtures of heavy 1-butene (12%) and light *cis*-2-butene (88%) were also co-isomerized at 3.5 cmHg in order to determine the main path in the interconversion from *cis*- to *trans*-2-butene.

Poisoning, IR and ESR Measurements. For poisoning experiment, the prepared catalyst was evacuated at 450 °C, equilibrated with a vapor of pyridine (0.5 cmHg) at room temperature for 30 min, evacuated again overnight at the same temperature and then heated *in vacuo* for 1—2 hr at different temperatures. The activities for the isomerization of 1-butene were examined after the above treatment. The isomerization was also carried out on the catalyst in the presence of NO (2.45 cmHg).

IR spectrum of the catalyst which was evacuated at 200 °C after exposed to pyridine vapor in *in situ* cell was measured at room temperature. ESR spectra of the catalyst with or without pyridine poisoning were measured at −195 °C before and after the introduction of 1-butene (5 cmHg) at 120 °C.

Results

Kinetics of the Isomerizations of n-*Butenes.* The time courses of the isomerizations of 1-butene and *cis*-2-butene are shown in Fig. 1. 1-Butene isomerized pre-

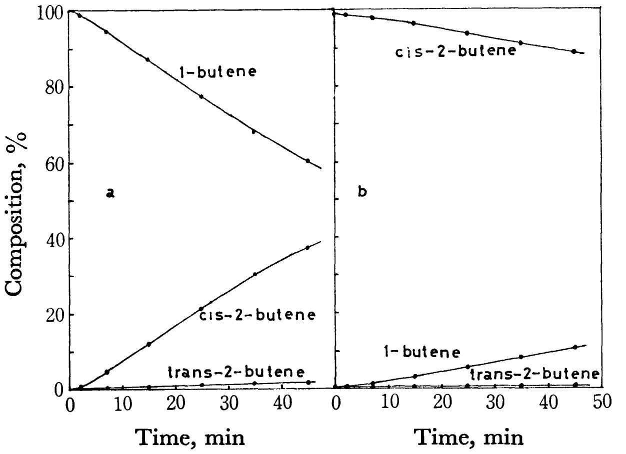

Fig. 1. Isomerization of 1-butene (a) and *cis*-2-butene (b) over TiO_2. Pressure of butenes: 11 cmHg.

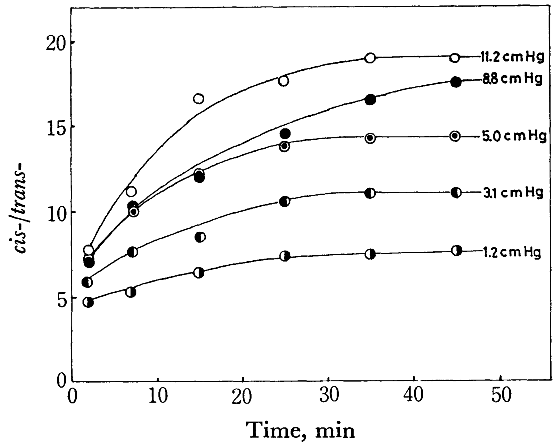

Fig. 2. Ratio of *cis*-2-butene/*trans*-2-butene in isomerization of 1-butene *vs.* reaction time at different pressures.

ferentially to *cis*-2-butene and *cis*-2-butene preferentially to 1-butene, in accord with the results observed by Shannon *et al.*[2] It is interesting that induction periods were observed in our case. Figure 2 shows the time course of the *cis-/trans-* ratio when 1-butene was isomerized over the catalyst at different pressures. The figure indicates the two remarkable features which have not been reported before for the isomerization of *n*-butene. The first one is that the *cis-/trans-* ratio becomes increasingly far from the equilibrium value as the isomerization progresses. The second one is that the higher the initial pressure, the larger the *cis-/trans-* ratio. Similarly, the increase in 1-/*trans-* ratio with reaction time and increasing initial pressure was observed for the isomerization of *cis*-2-butene.

The time courses of the *n*-butene isomerizations obeyed the reversible first order kinetics except the induction period. The initial rate, R_0, was calculated from the first order plots. Assuming that reactant butene is in adsorption equilibrium of Langmuir type and that the surface reaction of the adsorbed molecule is rate-determining, R_0, is given by the equation.

$$R_0 = kKP_0/(1+KP_0), \qquad (1)$$

where P_0 is the initial pressure of the reactant, K the

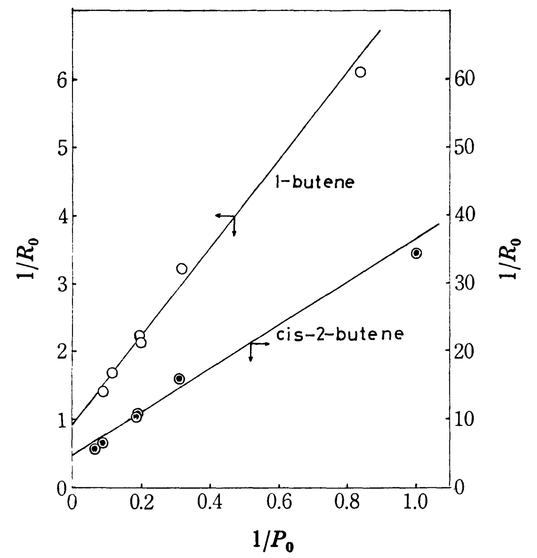

Fig. 3. Plots of reciprocals of initial rates against reciprocals of pressures for isomerizations of 1-butene and *cis*-2-butene.

adsorption constant of the reactant and k the rate constant of the surface reaction. In accord with the above equation, plots of the reciprocals of the initial rates against the reciprocals of reactant pressures were linear as shown in Fig. 3. The intercepts and slopes provided the adsorption constants (K_1 and K_c) of 1-butene and *cis*-2-butene. The adsorption constant of *trans*-2-butene could not be determined by the same way, because the reactivity of *trans* isomer was very low. In order to obtain the adsorption constant, the isomerization of 1-butene was carried out in the presence of different partial pressures of *trans* isomer, where the initial pressure of 1-butene was maintained at 5 cmHg. The initial rate, R_1, was calculated from the first order plots of the disappearance of 1-butene, where the amount of the products from the isomerization of *trans*-2-butene was neglected. The rate data were represented by the competitive reaction equation of Langmuir type.

$$R_{0(1)}/R_1 = K_tP_t/(1+K_1P_1) + 1, \qquad (2)$$

where P_1, P_t, K_1, and K_t are the initial pressures and the adsorption constants of 1-butene and *trans*-2-butene,

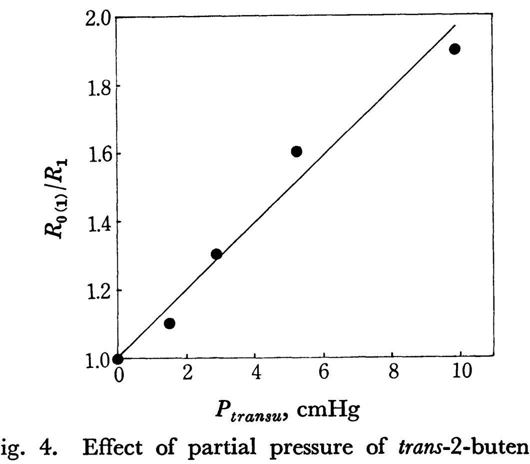

Fig. 4. Effect of partial pressure of *trans*-2-butene on initial rate of isomerization of 1-butene.

respectively. The plots of the Eq. (2) gave a straight line as shown in Fig. 4. K_t was calculated from the slope and K_1. Thus, K_1, K_c, and K_t were obtained to be 0.15 0.17, and 0.18 cmHg^{-1}, respectively.

Co-isomerization. From the results of the co-isomerization of a mixture of *cis*-2-C_4H_8 and *cis*-2-C_4D_8, isotope effects and intermolecular hydrogen exchange were determined. The data were analyzed by the method devised by Hightower and Hall.[5] For each isomer, the light fraction is given by the formula.

$$\frac{1}{2}N_4+\sum_{i=0}^{3}N_i \tag{3}$$

where N_i is the mole fraction of each isotopic species containing i deuterium atoms. The heavy fraction is then given by the formula.

$$\frac{1}{2}N_4+\sum_{i=5}^{8}N_i \tag{4}$$

The isotope effects were calculated from the relative activities of the two species; namely, the ratios of light materials to heavy materials in the products divided by the ratio in the starting materials.

TABLE 1. PRODUCT DISTRIBUTION FROM CO-ISOMERIZATION OF *cis*-2-C_4H_8 AND *cis*-2-C_4D_8 OVER TiO_2 AT 120 °C

	Composition of products	Isotopic composition, %								
		Light fraction					Heavy fraction			
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
1-C_4'	19.2	44.0	3.0	0	0	0	0	0.7	4.2	48.2
trans	8.9	65.5	3.0	0	0	0	0	0	3.6	27.9
cis	71.8	45.8	1.8	0	0	0	0	0	3.7	48.6

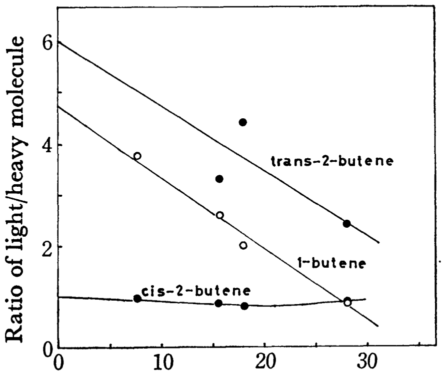

Fig. 5. Relative reactivities of *cis*-2-C_4H_8 and *cis*-2-C_4D_8 over TiO_2 at 120 °C.

Table 1 shows the isotopic distribution and Fig. 5 the ratio of light to heavy material for each isomer at various conversions. The data of Table 1 indicate that double bond migration and *cis-trans* isomerization are much faster than intermolecular H–D exchange. Evidently, both reactions do not involve the intermolecular exchange reaction, *i.e.*, the hydrogen transfers are intramolecular. Since the ratio of light molecule to heavy molecule in products represents kinetic isotope effect, Fig. 5 shows the existence of the large isotope effects, 4—5, in both isomerizations.

TABLE 2. POISONING WITH PYRIDINE AND NO

	No poison	pyridine[a]	pyridine[b]	pyridine[c]	NO	NO[e]
Activity	0.451	0	0.049	0.294	0.05[d]	0.294
$(cis/trans)_s$	15		13	16	4	9

Activity: cmHg min^{-1} g^{-1}, $(cis/trans\text{-})_s$: selectivity in a stationary state calculated from the plots analogous to Fig. 7.

a) Degassed at 200 °C for 2 hr. b) Degassed at 300 °C for 1 hr. c) Degassed at 400 °C for 1 hr. d) Poisoning occurred increasingly in progress of isomerizartion. e) After adsorption of NO (1.78 cmHg), the catalyst was degassed for 1 hr at 120 °C.

In the co-isomerization of a mixture of 1-C_4D_8 (12%) and *cis*-2-C_4H_8 (88%), the ratio of heavy molecule to light molecule in *trans*-2-butene was 0.093 at the stage of 2% formation of *trans*-2-butene, while the value in *cis*-2-butene was 0.019.

The Results of Poisoning and IR and ESR Spectra. The effects of poisoning with pyridine and NO on the isomerization of 1-butene are shown in Table 2, where the activities are the initial rates evaluated from the reversible first order plots. The catalyst on which pyridine was adsorbed showed no activity even after evacuation at 200 °C. By the poisoning with NO, the activity was decreased to less than one tenth. The selectivities were affected by poisoning with NO, but not with pyridine.

IR spectra of the catalyst poisoned with pyridine exhibited only the pyridine molecules coordinately bonded to the Lewis acid sites, in accord with the literatures.[6–8] ESR spectra of the above sample did not show the existence of dipyridil anion radical which was observed in the cases of the alkaline earth oxides.[9] The intensities of ESR signals[3] indicating Ti^{3+} for both catalysts with and without pyridine poisoning increased about four times on the introduction of 1-butene.

Discussion

Reaction Mechanism. The isomerization of 1-butene or *cis*-2-butene is known to give high ratio of *cis*-2-butene to *trans*-2-butene or 1-butene to *trans*-2-butene over basic catalysts such as MgO, CaO, Na–Al_2O_3 *etc.*[10–13] Since the adsorption constants of each butene isomer were almost the same in the present work, the basic feature of the selectivities, *i.e.*, the very high ratios of *cis*-/*trans*- and 1-/*trans*-, observed for TiO_2 seems not to result from a selective adsorption of *cis*-2-butene or 1-butene in the *cis* configuration on active sites, whose model was once presented for 1-butene isomerization over γ-Al_2O_3 by Gerberich and Hall.[14] In other words, the configurational differences among three isomers do not exert any influence on the adsorption of each isomer. The basic feature of the observed selectivity would result from the difference in the rate of interconversion among each isomer adsorbed on TiO_2.

The data on co-isomerization shown in Table 1 reveal that the hydrogen transfers involved in double bond migration and *cis-trans* isomerization are intramolecular. The large isotope effect observed for *cis-trans* isomerization does not reflect the effect for the direct interconversion step, because, in the co-isomerization of 1-C_4D_8 (12%) and *cis*-2-C_4H_8 (88%), the ratio of heavy to light molecule in *trans*-2-butene was larger than that in *cis*-2-butene. Actually, at a reaction temperature (200 °C) at which direct *cis-trans* interconversion becomes predominant, the isotope effect was not observed.2) Therefore, it is very likely that C–H bond cleavage is involved in the rate-determining step of the double bond migration. These features together with the high *cis*/*trans* ratio and slow direct *cis-trans* isomerization can be well explained only by a π-allyl anion mechanism,13) in which the *cis* allyl anion is thermodynamically more stable than the *trans* form and the *cis-trans* conversion is highly restricted.

Active Sites. The activity for the isomerization was completely lost by the adsorption of pyridine. Since pyridine was adsorbed on Lewis acid site to form its coordinately bonded molecule according to IR spectra and not on basic site (surface oxygen ion, O^{2-}) to form the dipyridyl anion9) according to ESR spectra, Lewis acid sites are considered to participate in active sites for the isomerization. On the other hand, the activity was considerably decreased by poisoning with NO, which is known to react with basic site (O^{2-}) to form nitrato-compound.15) These facts strongly suggest that the active sites consist of Lewis acid site–basic site pair. The concept that acid-base pair sites are active sites for the isomerization is also proposed for η-Al_2O_3 on the basis of the experiments on the reactivity of substituted olefins.16)

The active sites on TiO_2 prepared by calcining titanic acid *in vacuo* were previously reported to be Ti^{3+} formed by the reduction of Ti^{4+} on the surface.3) Since the activity of the present catalyst prepared by calcining titanic acid *in air* and then evacuated was decreased to two thirds of the activity by treating with dry air at 450 °C for 1 hr, the possibility that Ti^{3+} is a part of active sites can not be excluded. However, main active sites on the present catalyst are considered to be Lewis acid (Ti^{4+}) and oxygen ion (O^{2-}) pair. It should be emphasized that the main active sites on TiO_2 for the isomerization are varied by changing preparation condition of the catalyst.

Induction Period and Pressure Dependence of Selectivity.

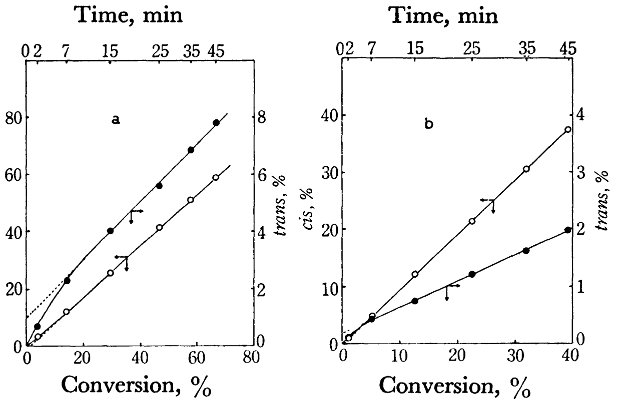

Fig. 6. Plots of each product isomers against conversion % for isomerization of 1-butene. Pressure of 1-butene: a) 1.2 cmHg, b) 11.2 cmHg.

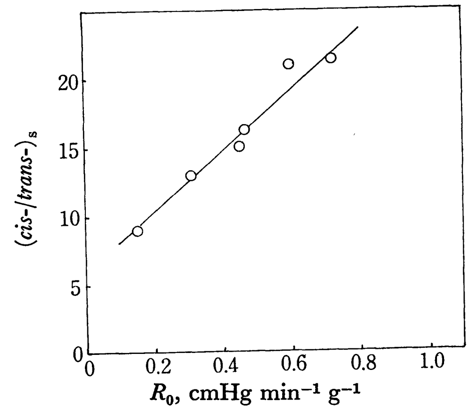

Fig. 7. Correlation between initial rates and selectivities of isomerization of 1-butene in a stationary state.

The remarkable results concerning selectivity and induction period found in the present work were not observed by Shannon *et al.*2) The difference is presumably due to the difference in the reaction conditions. They carried out the isomerization in a static system at a lower pressure (*ca.* 1.6 cmHg) and at higher temperatures (130—168 °C) than in our case. Only two examples of induction period have been reported for *n*-butene isomerization over solid catalysts. One is for Cu 13X zeolite17) and another for metal ion exchanged resin.18) In those cases, the induction period is considered to be caused by the reduction process of Cu^{2+} to Cu^+ or the complex formation of butene with metal ion, respectively. In our case, a part of Ti^{4+} was reduced to form Ti^{3+} by introducing 1-butene on both catalysts with and without pyridine poisoning. However, the catalyst poisoned with pyridine was completely inactive, though the catalyst without poisoning was active. Hence, the formation process of Ti^{3+} does not seem to cause the induction period.

The plots of % of *cis*- and *trans*-2-butene produced from 1-butene against the % conversion are shown in Fig. 6. The figure clearly indicates that a stationary state in selectivity is reached within 15 min, in accord with time-course curve in Fig. 1. The selectivities in a stationary state are obtained from the ratio of the slope for *cis*-isomer to that for *trans*-isomer in the linear parts. As shown in Fig. 7, the *cis*-/*trans*- ratio in a stationary state linearly increases with the rate in stationary state. As the initial rate obeyed the rate expression of Langmuir type, it is proportional to the adsorbed amount. Eventually, the larger the adsorbed amount of butenes is, the more the formation of *cis*-2-butene becomes predominant.

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