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Specific Catalysis of the *Cis–trans* Isomerization of Olefins by Sulfur Dioxide Adsorbed on Various Metal Oxides and Zeolites

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SO_2 adsorbed on solids inactive for the *n*-butene isomerization, such as NaX zeolite, porous Vycor glass, or silica gel, catalyzes selectively the *cis–trans* isomerization of 2-butenes at room temperature. On solids active for the reactions, such as γ-Al_2O_3, NiO, or α-Fe_2O_3, SO_2 poisons the double-bond migration, whereas it enhances the *cis–trans* isomerization. It was confirmed that the adsorbed SO_2 catalyzes neither the hydrogenation of *cis*-2-butene nor the hydrogen exchange reactions in the systems of C_2H_4–C_2D_4, *cis*-2-butene–C_2D_4, or *cis*-2-butene–deuterium, which was examined on NaX zeolite. The catalysis specific to the geometrical isomerization by adsorbed SO_2 was also observed in the case of 1,3-pentadiene. The formation of the polysulfone between SO_2 and 2-butenes was confirmed on MnO_2 and PbO_2. These catalysts show very high catalytic activity also for the geometrical isomerization of 2-butenes in the presence of SO_2.

The kinetic data on the geometrical isomerization of 2-butene and 1,3-pentadiene catalyzed by SO_2 are well interpreted by the mechanism that the *cis–trans* isomerization is accompanied by the copolymerization of SO_2 with olefin, i.e., addition and elimination of 2-butenes at the terminal of the polysulfone cause the isomerization of 2-butenes {*cis*- or *trans*-2-butenes $+ \cdot SO_2[\text{–}CH(CH_3)CH(CH_3)SO_2\text{–}]_n \rightleftarrows \cdot CH(CH_3)CH(CH_3)\text{–}SO_2[\text{–}CH(CH_3)CH(CH_3)SO_2\text{–}]_n$}. It is suggested that the polymerization may be initiated by the SO_2–olefin (1:1) charge transfer complex such as the one confirmed on the porous Vycor glass.

INTRODUCTION

Preliminary experiments showed that the SO_2 adsorbed on NaX zeolite, silica gel, or porous Vycor glass (PVG), possesses a considerable, highly selective, catalytic activity for the *cis–trans* geometrical isomerization of 2-butenes at room temperature. Without SO_2, these adsorbents do not catalyze either isomerization of 2-butenes, i.e., the double-bond migration and the *cis–trans* geometrical conversion (*1*). These results are very specific since it is the usual observation in the heterogeneous catalysis over metal oxides or zeolites that the geometrical isomerization of 2-butenes accompanies the double-bond migration to 1-butene or vice versa.

The result that SO_2 adsorbed on a solid surface possesses a potential ability to activate olefins at room temperature seems to be of significant information in the field of the air pollution chemistry, since the chemical reactions between SO_2 and olefins on a solid particulate have not been paid sufficient attention in polluted atmosphere.

Prior to considering a potential utility of SO_2 adsorbed on the solid surfaces as a catalyst or an actual importance in air pollution chemistry, we feel it necessary first to obtain more detailed information about the nature of the active species and the fundamental aspects of the geometrical isomerization of olefins catalyzed by SO_2 on the solid surfaces. Hence, in the present work, we have started a program of study in the following way. (a) The geometrical isomerization of 2-butenes caused by SO_2 was tested on various metal oxides and zeolites. (b) Hydrogenation of *cis*-2-butene or hydrogen exchange reactions in the systems of *cis*-2-butene–deuterium, *cis*-2-butene–C_2D_4, and C_2H_4–C_2D_4 were examined in the presence of SO_2 on NaX zeolite. (c) The uv spectra of the molecular complex between SO_2 and olefins were measured on the transparent porous Vycor glass. (d) The copolymerization of SO_2 with 2-butenes under the same reaction condition as that applied in the geometrical isomerization was studied on MnO_2 and PbO_2. (e) The kinetic investigation of the isomerization of 2-butenes and *cis*-1,3-pentadiene was carried out in the presence of SO_2 over NaX zeolite. Possible mechanism of the SO_2 catalyzing isomerization and the character of the active sites are considered along with these results.

EXPERIMENTAL METHODS

Apparatus. The apparatus employed was a conventional mercury free gas circulating system with 225 ml dead volume, capable of achieving a vacuum to 10^{-6} Torr. The pressure readings were made with a glass Bourdon's gauge.

Adsorbents. The solid adsorbents used for examining the catalysis of SO_2 were NaX zeolite (Linde 13X), porous Vycor glass (Corning 7930), SiO_2-60 and SiO_2-150 (both Merck Products), Na-mordenite and KL zeolite (obtained from Strem Chemical Inc.), NaHY zeolite [47% Na exchanged from NaY zeolite (Linde SK-40)], MnO_2 and PbO_2 (obtained from Wako Pure Chemical Co.), γ-Al_2O_3, NiO and α-Fe_2O_3. The γ-Al_2O_3, NiO and α-Fe_2O_3 were prepared by adding ammonia to the corresponding nitrate solutions, and the precipitates were washed by distilled water and calcined at 500°C for 2 hr.

Materials. The reagent SO_2 gas was the anhydrous grade of the Matheson Chemical Co. It was further purified by trap-to-trap distillation in a vacuum apparatus. The *cis*-2-butene was a high purity product of the Phillips Petroleum Co. The *trans*-2-butene, 1-butene and *cis*-1,3-pentadiene were purchased from Takachiho Kagaku Kogyo Co. or Wako Pure Chemical Co. Each compound was further purified by trap-to-trap distillation. The deuterium and C_2D_4 gas were the high purity products obtained from Takachiho Kagaku Kogyo Co. and were used without further purification.

Procedure. An adsorbent (0.1–0.3 g in usual case) was placed in the electrically heated quartz reactor, calcined at 500°C in dried oxygen and evacuated for 2 hr in vacuum below 5×10^{-5} Torr at the same temperature. The adsorbent thus treated was cooled in helium to a fixed temperature with a water bath *in situ*. After preadsorption of SO_2, the reaction was started by feeding and circulating 2-butene or 1,3-pentadiene gas through the catalyst bed. A small amount of reaction mixture was periodically collected and analyzed. The temperature of the water bath was controlled within ± 0.2°C.

Analysis. The isomers of *n*-butene and 1,3-pentadiene and the product of the *cis*-2-butene hydrogenation were analyzed by the gas chromatograph using a 4 mm $\times$ 7 m column with the stationary phase of propylene-carbonate on Celite 545. Reaction mixture of C_2H_4 and C_2D_4 was analyzed by applying infrared spectroscopy. The hydrogen-exchange products from the system of *cis*-2-butene–C_2D_4 and of *cis*-2-butene–deuterium were analyzed by mass spectrography. Electron spin resonance spectra of the adsorbents with SO_2 were taken at room temperature and at -196°C with a JEOL-PE-1X spectrometer. Ultraviolet spectra measurements of the adsorbed species were performed by using transparent porous Vycor glass plate as the adsorbent with a Shimazu UV-200 spectrometer. The spectra were recorded by placing the Vycor glass plate without SO_2 on it in the reference side of the light beam.

RESULTS

SO_2 catalysis in the geometrical isomerization of cis-2-butene over various solid adsorbents. NaX zeolite, silica gel, porous Vycor glass, Na-mordenite, KL zeolite, MnO_2 and PbO_2 in the presence of adsorbed SO_2 have shown catalytic activity for the *cis–trans* isomerization of 2-butenes at 24.5°C without inducing any double-bond migration to 1-butene. In the case of MnO_2 and PbO_2, the effect of SO_2 has been extremely emphasized among the adsorbents tested. Using 100% 1-butene as the starting material, it was confirmed that no double-bond migration occurs on NaX zeolite, porous Vycor glass and even on MnO_2 and PbO_2, the very active catalysts for the geometrical isomerization, in the presence of SO_2. Without SO_2, however, these seven adsorbents do not catalyze either reaction. NaHY zeolite, γ-Al_2O_3, NiO, and α-Fe_2O_3 catalyzed both reactions appreciably at 24.5°C in the absence of SO_2. Addition of SO_2 to these four oxides greatly enhanced the rate of *cis–trans* isomerization, but reduced the rate of double-bond migration. Several examples of the time course of the *trans*-2-butene formation from 100% *cis*-2-butene are shown in Fig. 1, where the SO_2 and the *cis*-2-butene introduced to the system are 5.4×10^{-4} and 9.0×10^{-4} mole, respectively. The rate of the isomerization decreases with the reaction time, which is generally observed on the oxides tested here. Some examples of the time course of the *cis*-2-butene isomerization in the absence of SO_2 are indicated in Fig. 2. The initial rates of both isomerizations with and without SO_2 are summarized in Table 1, where $R^0_{c\to 1}$ and $R^0_{c\to t}$ are the initial rates of the formation of 1-butene and of *trans*-2-butene from 100% *cis*-2-butene, respectively, and *n* denotes that no reaction was observed, i.e., the rate is less than 0.02×10^{-14} mole/cm^2 sec. It is clear that, on all the adsorbents tested, SO_2 catalyzes *cis–trans* isomerization and

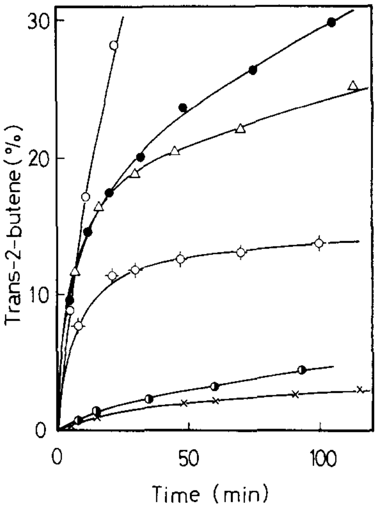


FIG. 1. Examples of the time course of the SO_2 catalyzing *cis–trans* isomerization over various solid adsorbents: (○) PbO_2 (0.059 g); (●) MnO_2 (0.027 g); (△) Al_2O_3 (0.409 g); (-◇-) NiO (0.301 g); (◑) NaX (0.368 g); (×) SiO_2-60 (0.414 g). No 1-butene was formed.

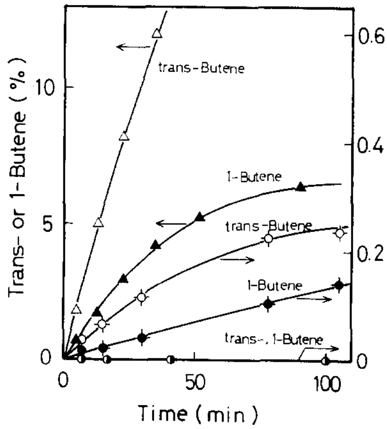


FIG. 2. Examples of the time course of the *cis–trans* isomerization and the double-bond migration in the absence of SO_2: (△, ▲), Al_2O_3 (0.394 g); (-◇-, -◆-), NiO (0.105 g); (◑), PbO_2 (0.307 g).

TABLE 1

Initial Rates of the *Cis–trans*-Isomerization and the Double-Bond Migration on Various Adsorbents at 24.5°C

Oxides or zeolites[a]	Surface area (m^2/g)	$R^0{}_{c\to 1} \times 10^{14}$ ($mole/cm^2$ sec)		$R^0{}_{c\to t} \times 10^{14}$ ($mole/cm^2$ sec)	
		Without SO_2	With SO_2	Without SO_2	With SO_2
NaX zeolite	425	n	n	n	1.65
PVG	144	n	n	n	1.06
SiO_2-60	285	n	n	n	1.50
SiO_2-150	122	n	n	n	2.19
Na-mordenite	322	n	n	n	0.22
KL zeolite	301	n	n	n	5.65
NaHY zeolite	556	1.12	0.87	2.18	9.57
γ-Al_2O_3	237	2.43	n	6.62	23.5
NiO	16.4	1.04	n	4.76	304
α-Fe_2O_3	29.0	1.79	n	1.28	21.1
MnO_2	113	n	n	0.20	897
PbO_2	13.0	n	n	n	3850

[a] The absorbents were evacuated in vacuum usually at 500°C (at 100°C for MnO_2 and PbO_2) prior to the run of experiment.

poisons double-bond migration. The results in Table 1 indicate that the enhanced rate of geometrical isomerization by adsorbed SO_2 does not necessarily correlate with the activity in the absence of SO_2 (see MnO_2 and PbO_2).

SO_2 catalysis to other reactions. The hydrogenation of *cis*-2-butene by deuterium was carried out at 24.5°C using 0.104 g of NaX zeolite with 31.6 μmoles of the adsorbed SO_2 under the pressure of 251 Torr of 1:1.4 mixture of deuterium and *cis*-2-butene. The reaction did not proceed at all even at the reaction time when 30.2% conversion to *trans*-2-butene was achieved. Mass spectroscopic analysis of the reacting mixture showed that no hydrogen of 2-butenes exchanged with deuterium.

The 1:1 mixture of *cis*-2-butene and C_2D_4 was fed to the NaX zeolite where SO_2 had been preadsorbed at 24.5°C, and the mixture was analyzed when the conversion of the geometrical isomerization of *cis*-2-butene reached to 26.0%. No hydrogen exchange between 2-butenes and C_2D_4 has been observed. The exchange in the system of C_2H_4–C_2D_4 was also examined, and the mixture was analyzed after the same reaction time. No exchange has been observed in this system either.

The isomerization of *cis*-1,3-pentadiene has been examined under the same reaction conditions applied to *cis*-2-butene. Similar to the results obtained in the case of *cis*-2-butene, only the *cis–trans* selective isomerization proceeded in the presence of adsorbed SO_2, whereas neither isomerization took place in the absence of SO_2.

Polysulfone formation between SO_2 and 2-butenes. The copolymerization of 2-butenes with SO_2 was tested on NaX zeolite, PVG, γ-Al_2O_3, MnO_2, and PbO_2 at 0°C by observing pressure decrease of 3.1×10^{-3} mole of the initial reaction mixture (1:1) of SO_2 and *cis*- or *trans*-2-butene. The formation of the polymer was further examined by infrared spectra measurement of the wafers of the catalysts after 5 hr reaction. It was confirmed that the copolymerization occurs only on MnO_2 and PbO_2; both catalysts have very high catalytic activity for *cis–trans* isomeriza-

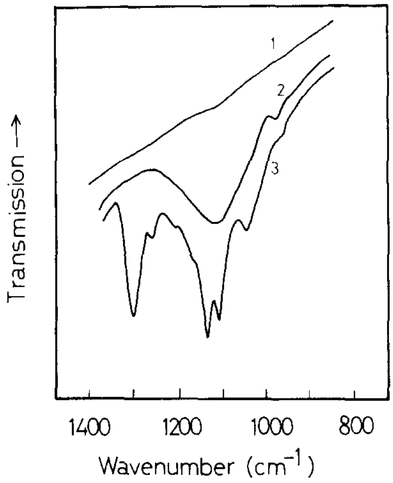


FIG. 3. Infrared spectra of the wafers of MnO_2 after the reaction at 0°C: (1) the background spectrum of MnO_2; (2) after 5 hr contact with SO_2. The very broad band at 1120 cm^{-1} may be due to the oxidized species of SO_2 on the surface; (3) after 5 hr contact with the mixture gas of SO_2 and *cis*-2-butene. The bands at 1050, 1105, 1140, 1220, 1260, and 1300 cm^{-1} are due to the polysulfone (*31*).

tion of 2-butenes in the presence of SO_2 (Table 1). The formed polymer gives two characteristic absorption bands of the polysulfone as shown in Fig. 3, one at 1300 cm^{-1} and the other at 1105–1140 cm^{-1} due to the symmetrical and the unsymmetrical stretching vibration of the sulfone group, respectively. No difference was observed in the spectra between the polysulfone of *cis*-2-butene and that of *trans*-2-butene. It was estimated that 0.77 $\times 10^{-4}$ and 0.95 $\times 10^{-4}$ mole of the reactants, for SO_2–*cis*-2-butene and for SO_2–*trans*-2-butene system, respectively, were converted to the polysulfone after 5 hr reaction on 0.30 g of MnO_2. The rate of the copolymerization decreases with time as the similar trend observed in the rate of geometrical isomerization.

The molecular complex between SO_2 and olefin on the porous Vycor glass. Figure 4a shows the differential uv spectra of the porous Vycor glass with the adsorbed SO_2 and *cis*-2-butene with reference to the glass without SO_2 and *cis*-2-butene. Figure 4b shows the spectra for the SO_2–2,3-dimethyl-2-butene system. The new absorption bands appeared, following the coadsorption of SO_2 and olefin, at the wavelength 230–260 and 300–400 nm for *cis*-2-butene, and at 320–420 nm for 2,3-dimethyl-2-butene. In the latter case, the absorption maximum is clearly seen at about 345 nm. Booth *et al.* have reported the spectra of the complexes between SO_2 and olefins (1:1) in *n*-hexane solvent. Their data show the two absorption maxima for the SO_2–*cis*-2-butene system at 262 and 295 nm. The former is attributed to the charge-transfer absorption by the complex, and the latter to the enhanced absorption of the transition of sulfur dioxide at 290 nm brought about by the proximity of the π-donating *cis*-2-butene molecule. In the case of 2,3-dimethyl-2-butene, the complex shows the absorption maximum at 325 nm (*2*). The new absorptions observed on the porous Vycor glass can be assumed to be the similar ones obtained in the liquid phase by Booth *et al.* (*2*), i.e., the 230–260 nm band for SO_2–*cis*-2-butene and 320–420 nm band for SO_2–2,3-dimethyl-2-butene are attributed to the charge transfer complex formed on the solid surface between SO_2 and the respective olefin. The long tailing

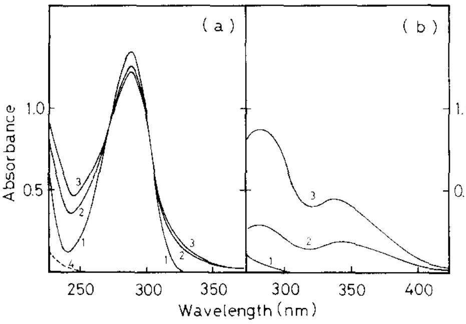


FIG. 4. Ultraviolet spectra of the SO_2–olefin molecular complex on PVG: (a) (1) SO_2 only (10.4 Torr); (2): (1) +*cis*-2-butene (5.8 Torr); (3): (1) +*cis*-2-butene (27.3 Torr); (4) *cis*-2-butene only (5.8 Torr); (b) (1) 2,3-dimethyl-2-butene only (<0.05 Torr); (2): (1) +SO_2 (2.1 Torr); (3): (1) +SO_2 (6.4 Torr).

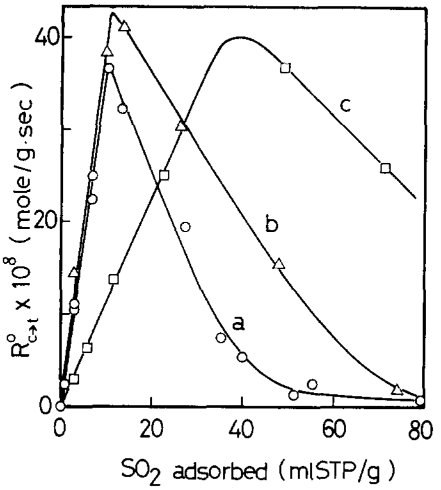


FIG. 5. Plot of the rate of the *cis–trans* isomerization vs the amount of SO_2 adsorbed on NaX zeolite: starting olefin: (a) *cis*-2-butene (at 24.5°C); (b) *cis*-2-butene (at 60°C); (c) *cis*-1,3-pentadiene (at 24.5°C).

band at 300–400 nm for SO_2–*cis*-2-butene system must be caused by the absorption of SO_2 enhanced by *cis*-2-butene.

Kinetic data on NaX zeolite. SO_2 adsorbs on NaX zeolite at 24.5°C more than 70 ml STP/g with a trace of residual SO_2 in gas phase. The preferential adsorption of SO_2 has been observed in the mixture of SO_2 and *cis*-2-butene, i.e., the preadsorbed *cis*-2-butene was desorbed and its place was taken by the introduced SO_2. Hence, under experimental conditions applied for the kinetic studies, the amount of SO_2 remaining in gas phase can be neglected. The relation between the initial rate of *cis* to *trans* isomerization, $R^0_{c\to t}$, and the amount of adsorbed SO_2 is indicated in Fig. 5, where (a) and (b) are the results of *cis* to *trans* isomerization using *cis*-2-butene as the starting material at 24.5 and 60°C, respectively, and (c) is the result of *cis*-1,3-pentadiene at 24.5°C. The reactions were carried out under the pressure of the olefins at 125 ± 3 Torr. The initial rate was calculated from the slope of the conversion-time course at the reaction time of 10 min, and the conversion to the *trans*-isomer at the time was controlled less than 1% by changing the amount of the adsorbent. It is shown in Fig. 5 that $R^0_{c\to t}$ increases proportionally with the amount of adsorbed SO_2 at the amount of SO_2 less than ~10 ml STP/g for *cis*-2-butene and ~40 ml STP/g for *cis*-1,3-pentadiene. Over these amounts of SO_2, the rates drop steeply with increasing the amount of SO_2.

Figure 6 shows the effect of the initial pressure of *cis*-2-butene, $P_{cis\text{-}Bu}$, on $R^0_{c\to t}$ at 24.5°C under the different amount of the adsorbed SO_2, 2.9 ml STP/g for curve (a) and 40.0 ml STP/g for curve (b).

The Arrhenius plots of the initial rates of the isomerization for 2-butenes and *cis*-1,3-pentadiene are indicated in Figs. 7 and 8, respectively. Both $R^0_{c\to t}$ and $R^0_{t\to c}$ for the 2-butene isomerization show their maxima at about 40°C. From the portion of the straight line in Fig. 7, the activation energies for the 2-butenes are 7.8 ± 0.3 and 11.4 ± 0.4 kcal/mole for *cis* to *trans* and *trans* to *cis*, respectively. In the case of 1,3-pentadiene, the Arrhenius plot of the $R^0_{c\to t}$ gives the good straight line in the temperature range 0 to 60°C, and the activation energy is obtained as 11.0 ± 0.3

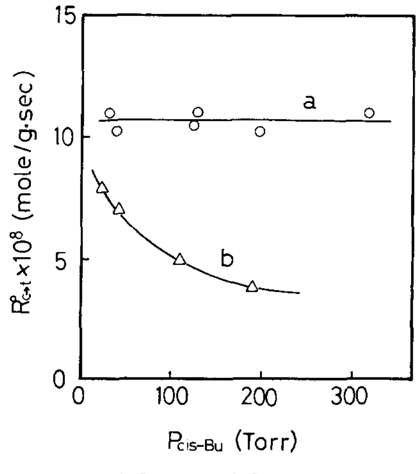


FIG. 6. Plot of the rate of the *cis–trans* isomerization vs the pressure of *cis*-2-butene on NaX zeolite: (a) amount of SO_2 adsorbed = 2.9 ml STP/g; (b) amount of SO_2 adsorbed = 40.0 ml STP/g.

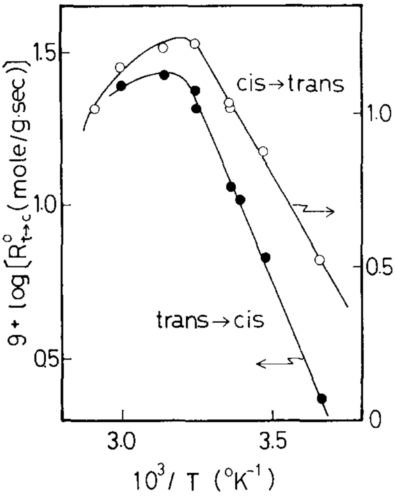


FIG. 7. Arrhenius plot of the rate of the *cis–trans* isomerization of 2-butenes on NaX zeolite: (○) $P_{cis\text{-Bu}} = 128 \pm 3$ Torr, and the amount of SO_2 adsorbed is 3.0 ml STP/g; (●) $P_{trans\text{-Bu}} = 105 \pm 3$ Torr, and the amount of SO_2 adsorbed is 6.0 ml STP/g.

kcal/mole. The decrease in the rate observed for 2-butene isomerization at above 40°C may be due not to the desorption of the adsorbed SO_2 but to the desorption of the 2-butenes from the active sites, because the decrease was not observed in the case of 1,3-pentadiene.

During the progress of the reaction, the temperature of the reaction bed was suddenly jumped at the time of 60 min, and the rates of the isomerization were measured just before and after the temperature jump. The experiment was carried out under the same reaction conditions applied for the data in Figs. 7 and 8, and the conversion was less than 3% at the jump. The apparent activation energies, E_a, calculated from the rates before and after the jump, have been plotted against the temperature in Fig. 9 for the case of 2-butenes, where the tail and the head of the arrow indicate the temperature before and after the jump, respectively. E_a for the 2-butenes are all 5–10 kcal/mole larger than the activation energies estimated at the corresponding temperature range in Fig. 7. On the other hand, E_a for 1,3-pentadiene obtained lie within 12.1 ± 2.3 kcal/mole irrespective of the temperature range, which are approximately same within the experimental error as that calculated from Fig. 8 (11.0 ± 0.3 kcal/mole).

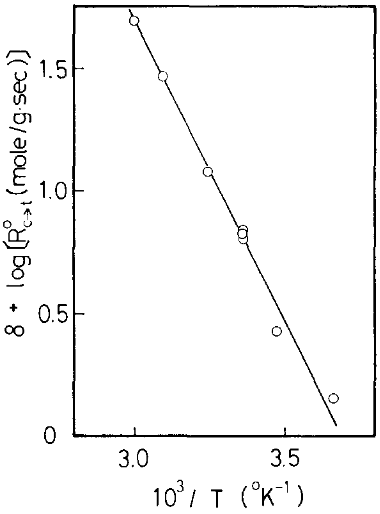


FIG. 8. Arrhenius plot of the rate of the isomerization of *cis*-1,3-pentadiene on NaX zeolite: the pressure of *cis*-1,3-pentadiene is 128 ± 3 Torr and the amount of adsorbed SO_2 is 5.8 ml STP/g.

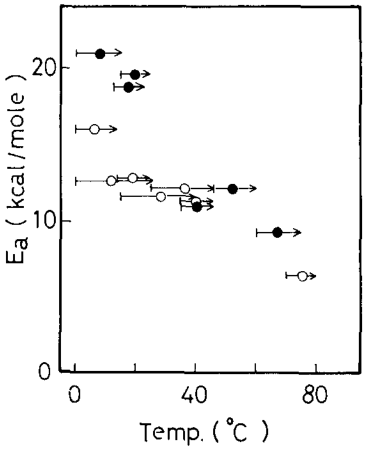


FIG. 9. Activation energy obtained by the temperature jump method at various temperatures on NaX zeolite (2-butenes): (●) *trans* to *cis*; (○) *cis* to *trans*.

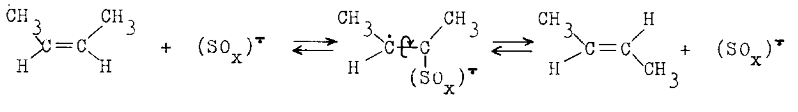
DISCUSSION

The active site and the possible mechanism. The catalytic isomerization of *n*-butenes over oxides or zeolites has been extensively studied in attempts to understand the reaction mechanism and the nature of the active site. On acid catalysts the mechanism involving carbonium ion formation on Brönsted or Lewis acid site is generally accepted (*3–8*). On basic catalysts, the reaction is believed to proceed via an allylic carbanion as a reaction intermediate (*9–11*). Other reaction intermediates proposed are π-bonded allylic species over zinc oxides (*12*), or alkyl radicals formed by the addition of hydrogen to the double bond usually found for *n*-butene isomerization over metal catalysts (*13*). Whatever mechanisms mentioned above are considered, it is the usual case that the geometrical isomerization of 2-butenes accompanies the double-bond migration. Although in some cases it was shown that the exchange of deuterium with olefins and the isomerization were completely independent reactions (*14*), extensive deuterium–olefin exchange and isotopic scrambling of d_x-olefin–d_0-olefin are usually observed over the metal oxides active for the *n*-butene isomerization.

In this work, it was confirmed that the adsorbed SO_2 is effective in catalyzing only on the *cis–trans* geometrical isomerization with poison for double-bond migration; no deuterium exchange reactions of deuterium–*cis*-2-butene, C_2D_4–*cis*-2-butene or C_2D_4–C_2H_4 occur. These results show that the geometrical isomerization induced by adsorbed SO_2 does not proceed with the mechanisms generally believed on metal oxides.

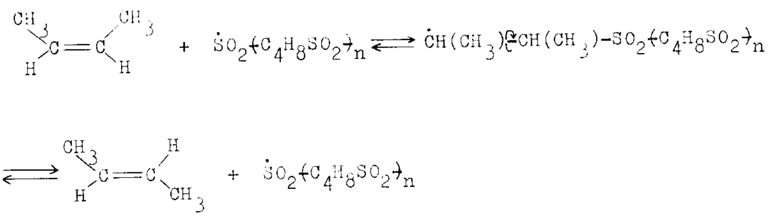
Possible mechanisms that can explain our results are discussed as follows:

I. The reaction may proceed via 2-butyl radical formed by the interaction of 2-butene with radical species such as SO_2^-, SO_3^- or SO_4^-.



The selective *cis–trans* isomerization via 2-butyl radical is generally proposed in the homogeneous catalysis of NO_2 (*15*), NO (*16*), I (*17*), or RS (*18*), and in the heterogeneous catalysis by siloxene (*19*). The formation of SO_3^- or SO_4^- has been shown on MgO (*20*) or partially reduced vanadium(V) oxide on silica gel (*21*). However, the formation of these radicals on the inactive catalysts such as silica gel, porous Vycor glass or NaX zeolite seems very unlikely even in the presence of molecular oxygen. As a matter of fact, even a trace of esr signal caused by these radicals was not found for these three catalysts. It was shown that SO_2^- radical is produced easily on Al_2O_3 and various cation-exchanged Y zeolites (*22*) and NaX zeolite (*23*). The formation of SO_2^- radical was confirmed also on the NaX zeolite used in the present work at room temperature. This signal shows $g_{\parallel} = 2.010$ and $g_{\perp} = 2.002$. It is not likely, however, that SO_2^- is the active species causing the geometrical isomerization of 2-butenes, because no SO_2^- radical has been produced on the silica gel and the porous Vycor glass, but the rates of the geometrical isomerization catalyzed by SO_2 on these adsorbents lie in the same order of magnitude as that obtained on the NaX zeolite (Table 1).

II. The reaction may take place via the elimination of the terminal 2-butyl radical of the formed polysulfone.



In liquid SO_2, the geometrical isomerization of 2-butenes accompanying the polysulfone production has been shown by Dainton and Bristow (*24, 25*). The formation of the polysulfone from SO_2 and *cis*-2-butene has been confirmed in the present work on MnO_2 and PbO_2 at 0°C as mentioned above. The rates of the geometrical isomerization of *cis*-2-butene catalyzed by the adsorbed SO_2 are extremely high for these two oxides compared with the other adsorbents (Table 1). It has been suggested that the geometrical isomerization of various olefins always requires the production of polysulfone on MnO_2 (*26*). Hence, we propose that the active species causing the geometrical isomerization of 2-butene and 1,3-pentadiene over the solid adsorbents is the active polysulfone formed from SO_2 and the respective olefin.

Explanation of the kinetic data. It is probable that the formed polysulfone in the narrow pores of NaX zeolite (diameter of the supercage is ~13 Å, and that of the main channel ~8 Å) would block the passing of butene molecules through the main channels of the zeolite, and this effect cannot be ignored especially under high concentration of the adsorbed SO_2. We consider this is the reason for the decrease in the isomerization rate at high concentration of SO_2 (Fig. 5). With NaX zeolite, however, the attempt to confirm the formation of the polysulfone of SO_2 and *cis*-2-butene has been unsuccessful, because the very small number of active sites may be present on the surface, accordingly, a small number of the polymer only is allowed, or the formation of the long chain polymer in the narrow pores of NaX zeolite may be prohibited.

It has been shown that the copolymerization of SO_2 with *n*-butenes in liquid phase has the ceiling temperature at around room temperature (*27–29*). This has been confirmed also in the gas–solid heterogeneous phase over MnO_2 (*26*). Furthermore, the copolymerization of SO_2 with *cis*-2-butene over this oxide occurs readily, but none with *cis*-1,3-pentadiene (*26*). If the same sequences are true on NaX zeolite, the retardation on the reaction due to the polysulfone produced explains the result of the smaller negative slope of curve (b) for 60°C than the slope of curve (a) for 24.5°C in Fig. 5 because of the slower production of the polymer at the higher reaction temperature. Furthermore, the easier formation of polysulfone with *cis*-2-butene than with 1,3-pentadiene explains (i); the larger negative slope of curve (a) for *cis*-2-butene than curve (c) for 1,3-pentadiene, and (ii); the amount of SO_2 giving the maximum rate is smaller with *cis*-2-butene than with *cis*-1,3-pentadiene (see Fig. 5).

At low concentration of adsorbed SO_2, $K^0_{c\rightarrow t}$ does not depend on the pressure of butene, though at high SO_2 concentration the rate decreases with increasing the pressure (Fig. 6). The latter result can be also interpreted qualitatively by the effect of the formed polymer, since the accumulation of polysulfone must increase with the pressure of *cis*-2-butene. The retardation by the polymer, however, can be neglected at the earlier stage of the reaction under low concentration of SO_2.

Anomalously high activation energies for

2-butenes obtained by the temperature jump method can be explained by the unstability of the polysulfones at around room temperature (*27–31*), i.e., the number of active polymers is increased after the temperature jump by the decomposition of the accumulated polymers in the reaction time of 60 min, which resulted in the estimation of the too high apparent activation energy. On the other hand, in the case of 1,3-pentadiene, the agreement between the activation energy obtained from the initial rate (Fig. 8) and that from the temperature jump method suggests that, in contrast to 2-butenes, the polysulfone of 1,3-pentadiene may not be formed appreciably, which is supported by the result that a negligible formation of polysulfone of 1,3-pentadiene has been confirmed on MnO_2 (*26*).

The mechanism and the rate expression. As mentioned above, the kinetic data for 2-butene isomerization are well explained by considering the effect of the polysulfone formation, and it is suggested that the geometrical isomerization proceeds by mechanism (II). The very general observation of the SO_2 catalyzing geometrical isomerization of 2-butenes on every catalyst tested in this work, independent of the original activity of the catalysts in the absence of SO_2, implies that the active species initiating the reaction is the charge-transfer complex (CTC) formed generally over solid adsorbents from the physically adsorbed SO_2 and 2-butenes, such as the one observed on the porous Vycor glass. The complex migrating into a localized electrostatic field of the surface ions may be strongly polarized and activated.[1] Thus, we propose here a general scheme for the SO_2 catalyzing isomerization of olefins on the gas–solid interface by referring to the mechanism suggested in liquid SO_2 (*24, 25*).

$$SO_2(a) + cis\text{-}Bu(a) \overset{K}{\rightleftarrows} CTC(a), \qquad (1)$$

$$CTC(a) + CTC(a) \rightarrow P_B(a) + P_S(a), \qquad (2)$$

$$P_B(a) \rightarrow P_S(a) + trans\text{-}Bu(a), \qquad (3)$$

$$\rightarrow P_S(a) + cis\text{-}Bu(a), \qquad (4)$$

$$P_S(a) \rightarrow P_B(a) + SO_2(a), \qquad (5)$$

$$P_B(a) + SO_2(a) \rightarrow P_S(a), \qquad (6)$$

$$P_S(a) + cis\text{-}Bu(a) \rightarrow P_B(a), \qquad (7)$$

$$P_S(a) + P_B(a) \rightarrow \text{stabilized}, \qquad (8)$$

where, the mechanism is considered under the low conversion of the isomerization using 100% *cis*-2-butene as the starting olefin, the symbol (a) denotes the adsorbed state on the surface, and P_B and P_S are the terminal group of 2-butyl and SO_2 radical of the active polymer, respectively

$$[P_B \rightarrow \dot{C}H(CH_3)CH(CH_3)SO_2\text{---}$$
$$CH(CH_3)CH(CH_3)\dot{S}O_2 \leftarrow P_S].$$

The charge-transfer complex (CTC) initiates the reaction by Eq. (5) in the vicinity of the surface ions. It may be possible that the propagation of polymer takes place also by the CTC as Eqs. (6′) and (7′):

$$P_B(a) + CTC(a) \rightarrow P_B(a), \qquad (6')$$

$$P_S(a) + CTC(a) \rightarrow P_S(a). \qquad (7')$$

The steady state approximation of P_S and P_B with Eqs. (1)–(8) gives the following rate expression.

$$R^0_{c\rightarrow t} = k_3 \left(\frac{k_2(k_5 + k_7[cis\text{-}Bu(a)])}{k_8(k_3 + k_4 + k_6[SO_2(a)])} \right)^{\frac{1}{2}} \times K[cis\text{-}Bu(a)][SO_2(a)]. \qquad (9)$$

Considering that the active site is saturated by *cis*-2-butene at 24.5°C under the pressure range applied in the kinetic studies

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[1] The SO_2 catalyzing isomerization has been studied over various cation-exchanged X zeolite at low concentration of adsorbed SO_2. The rate of the isomerization increases with the strength of the electrostatic field of the metal cations in the zeolites, which supports the idea that the charge-transfer complex initiates the reaction by being polarized in the vicinity of the surface cations (*32*).

[Fig. 6, curve (a)], and assuming $k_3 + k_4 \gg k_6[SO_2(a)]$ at the low concentration of adsorbed SO_2, Eq. (9) will be

$$R^0_{c\to t} = k[SO_2(a)], \quad k = \text{constant}, \qquad (10)$$

which is the same equation as that obtained experimentally at the low concentration of adsorbed SO_2 where the retardation by the polymer can be neglected.

The unimolecular initiation with CTC instead of Eq. (2) also satisfies the experimental rate equation by assuming the unimolecular termination of P_S or P_B instead of Eq. (8). However, the kinetic data described here are not sufficient to provide a quantitative test on this point.

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