The *cis-trans* Isomerization of 2-Butenes Caused by Sulfur Dioxide Adsorbed on Porous Vycor Glass. The Contribution of the Charge-transfer Complex

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Sulfur dioxide adsorbed on porous Vycor glass enhances the *cis-trans* isomerization of 2-butenes selectively, but it poisons the double-bond migration. The correlation between the *cis-trans* isomerization and the sulfur dioxide–*cis*-2-butene charge-transfer complex observed on the glass were studied under various pressures of the reactants. The kinetic data of the reaction were well explained by the reaction mechanism in which the isomerization occurs *via* the addition and elimination of 2-butene molecules at the terminal of the polysulfone formed from sulfur dioxide and *cis*-2-butene in the adsorbed layer. It has been suggested that the copolymerization is initiated through the charge-transfer complex polarized in the strong electrostatic field of the exposed aluminum ions contained in the glass.

Porous Vycor glass, evacuated at a high temperature (>500 °C), is catalytically inactive for the isomerization of normal butenes at room temperature. However, the addition of a small amount of sulfur dioxide causes a considerably fast *cis-trans* isomerization of 2-butenes very selectively. In the gas phase, of course, sulfur dioxide exerts no effect upon the butene isomerization. Similar specific catalyses of the sulfur dioxide manifested in the adsorbed layer of various solid adsorbents have been reported in previous papers,[1,2] and it has been suggested that the geometrical isomerization of 2-butenes takes place by means of a mechanism in which the addition and subsequent elimination of the *cis*- or *trans*-2-butene molecule at the terminal of the formed polysulfone cause the isomerization. It has been suggested that the polysulfone formation may be initiated by the sulfur dioxide–olefin (1 : 1) molecular complex,[2] though the kinetic data obtained over NaX zeolite[2] could not be tested in this point by observing the presence of the complex by means of ultraviolet spectroscopy because of its opacity in the ultraviolet-wavelength region.

In order to carry out a quantitative test of the contribution of the molecular complex, we have chosen porous Vycor glass as the adsorbent because of its good transparency in the wavelength range down to ≈ 210 nm. In the present work, we will first carry out a kinetic investigation of the geometrical isomerization of *cis*-2-butene over porous Vycor glass in the presence of sulfur dioxide. Then, examining the molecular complex in the adsorbed layer of the glass by means of the ultraviolet spectroscopic method, we intend to verify that the complex plays a significant role in the reaction. Finally, the nature of the active site on the glass will be discussed along with the kinetic data obtained over glass evacuated at various temperatures.

Experimental

Materials. The porous Vycor glass used was a glass plate (Corning No. 7930, surface area 150 m^2/g) $30\times8\times0.8$ mm in size. Similar samples were shown to contain ≈3% of B_2O_3, ≈0.4% of Al_2O_3, and less than 0.2% of Na_2O and K_2O inaddition to silica [information supplied by Corning Glass Works]. After having been calcined thoroughly at 700 °C in air, the glass was washed by distilled water and dried at 400 °C; then it was placed in the reactor.

The sulfur dioxide reagent was of an anhydrous grade of the Matheson Chemical Company. The *cis*-2-butene was a high-purity product of the Phillips Petroleum Company. The stated purity of 99.9% for *cis*-2-butene was verified by gas chromatography. Each compound was further purified by trap-to-trap distillation in a vacuum apparatus.

Apparatus. The appratus employed was a conventional mercury-free and grease-free gas-circulating system with a dead volume of 288 ml, capable of achieving a vacuum down to 10^{-6} Torr. A part of the reactor, where the glass was placed, was constructed from a quartz cell ($10\times10\times40$ mm) designed for spectrophotometric use. The pressure readings for the reactants were made with a glass Bourdon gauge.

Procedure. Prior to every run of the experiment, the glass placed in the reactor was calcined at 600 °C in dried oxygen and then evacuated for 2 h in a vacuum below 5×10^{-5} Torr at the same temperature. After introducing sulfur dioxide at 25 °C, the reaction was started by feeding in *cis*-2-butene and circulating the mixture gas through the reactor. A small amount of reacting gas was periodically collected and analyzed by gas chromatography. The temperature of the reactor was controlled within ±0.2 °C by using a water bath. The ultraviolet-spectra measurements were performed by means of a Shimadzu UV-200 spectrometer. The spectra were recorded by placing the glass without any adsorbate on the reference side of the light beam.

Results

The geometrical Isomerization of cis*-2-Butene Enhanced by Sulfur Dioxide.* Porous Vycor glass calcined in a vacuum at 600 °C exhibits a low catalytic activity in the two isomerizations of *cis*-2-butene, *i.e.*, the geometrical isomerization to *trans*-2-butene and the double-bond isomerization to 1-butene, at 25 °C. The initial rates of the former and latter reactions were 7.23×10^{-8} and 15.0×10^{-8} mol/g min respectively, at an initial pressure of *cis*-2-butene of 46 Torr.

The addition of a small amount of sulfur dioxide to the reaction system markedly enhanced the rate of geometrical isomerization, but it stopped the double-bond migration. Furthermore, no double-bond migration in the presence of sulfur dioxide was confirmed by using 100% 1-butene as the starting olefin.

The effects of the pressure of sulfur dioxide and *cis*-2-butene on the initial rate of the *trans*-2-butene

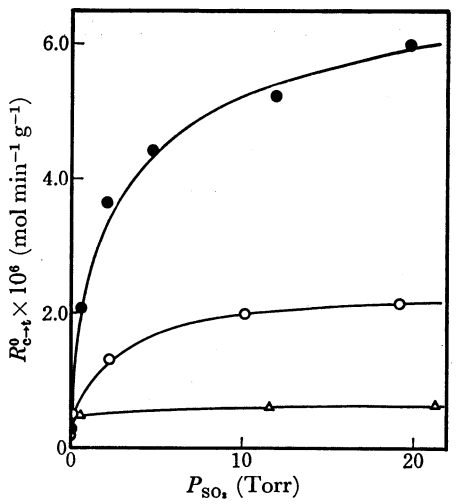

Fig. 1. Effect of the pressure of sulfur dioxide on the rate of geometrical isomerization: The pressure of *cis*-2-butene: (●), 107 Torr; (○), 6.2 Torr; (△), 0.9 Torr.

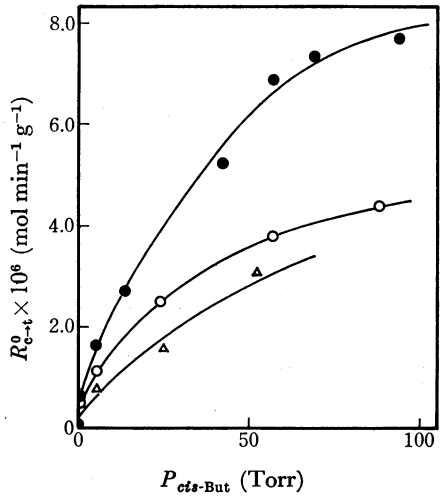

Fig. 2. Effect of the pressure of *cis*-2-butene on the rate of the isomerization: The pressure of sulfur dioxide: (●), 51 Torr: (○), 4.9 Torr; (△), 2.0 Torr.

formation, $R^0_{c\to t}$, at 25 °C are shown in Figs. 1 and 2. These figures exhibit that $R^0_{c\to t}$ can not be expressed by a simple function of the pressures of the two compounds.

The Charge-transfer Complex of Sulfur Dioxide with cis-*2-Butene.* Examples of the ultraviolet spectra of the glass with *cis*-2-butene, sulfur dioxide, and the two compounds adsorbed together on the glass are shown in Fig. 3. The (c)spectrum, taken 3—5 min after the coadsorption of sulfur dioxide and *cis*-2-butene, indicates new absorptions at around 240 and 330 nm. The absorbance of the spectra at wavelengths less than ≈250 nm increases with the time, as can be seen in the figure (Spectra(c)—(f)). After various durations of the coadsorption, the glass was evacuated in a vacuum for 2 h at 25 °C. The spectra of the glass taken after this treatment are shown in Fig. 4. The absorption due to adsorbed sulfur dioxide has disappeared after the evacuation, though a considerable portion of the spectra seen at the wavelengths less than ≈240 nm still remains.

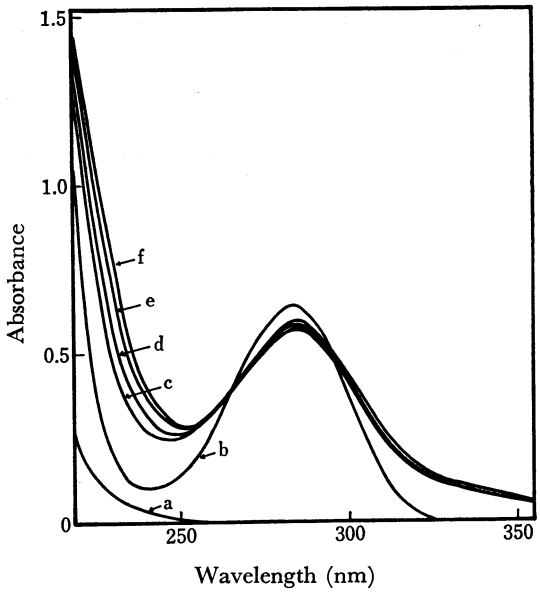

Fig. 3. The UV-spectra of the compounds adsorbed at 25 °C on the porous Vycor glass. (a) *cis*-2-butene (amount of adsorption is 2.40 ml STP/g); (b) sulfur dioxide (0.45 ml STP/g); (c)—(f) sulfur dioxide (0.45 ml STP/g) and *cis*-2-butene (2.4 ml STP/g) coadsorbed. The spectra (c)—(f) were recorded at various times after the addition of the both compounds: (c) 3—5 min, (d) 12—14 min, (e) 40—42 min, (f) 108—110 min. Scanning speed was 100 nm/min, scanning wavelength from 400 to 200 nm.

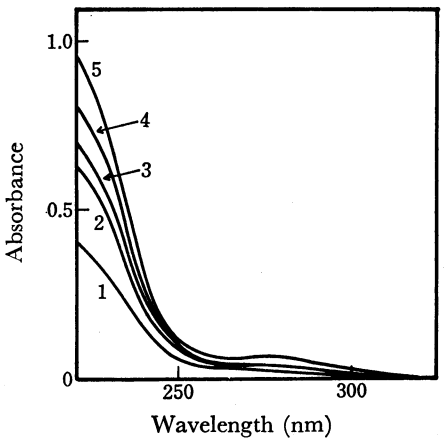

Fig. 4. The UV-spectra of the compound remained on the glass after the evacuation for 2 h: Sulfur dioxide and *cis*-2-butene had been coadsorbed before the evacuation for the following time; (1) 8 min, (2) 20 min, (3) 38 min, (4) 105 min, (5) 930 min.

It is assumed that the increase in the absorbance with the time for the spectra in Fig. 3 results from the accumulation of the unknown compounds, referred to as P_x hereafter, which corresponds to the spectra in Fig. 4. The D_{ctc} at various wavelengths, defined by the following equation (i):

$$D_{ctc} = D_{ob} - D_{SO_2} - D_{But} \quad \text{(i)}$$

are plotted against the duration of coadsorption, where D_{ob}, D_{SO_2}, and D_{But} are the optical density of the total absorption observed in the case of coadsorption

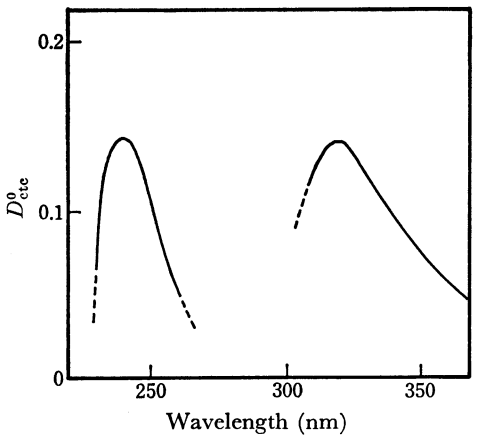

Fig. 5. Plot of D^0_{ctc} against wavelength.

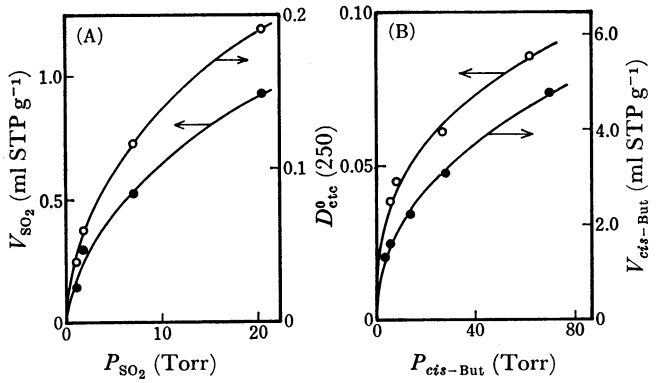

Fig. 6. (A) Plot of D^0_{ctc} (250) (open circles) and the amount of adsorbed sulfur dioxide (V_{SO_2}) (closed circles) against the pressure of sulfur dioxide: $P_{cis\text{-But}}$ =6.2 Torr. (B) Adsorption isotherm of *cis*-2-butene (closed circles) and the plot of D^0_{ctc} (250) against the pressure of *cis*-2-butene (open circles): P_{SO_2}=4.9 Torr.

(Spectra(c)—(f) in Fig. 3), the optical density for the sulfur dioxide (Spectrum(b)), and that for the *cis*-2-butene (Spectrum(a)) respectively. In order to exclude the contribution of P_x, the extrapolated values of D_{ctc} to the zero duration time of adsorption, D^0_{ctc}, were estimated. They are plotted against the wavelengths in Fig. 5.

The effects of the pressures of sulfur dioxide and *cis*-2-butene on D^0_{ctc} at 250 nm are indicated by open circles in Fig. 6. The adsorption isotherm of sulfur dioxide in the presence of *cis*-2-butene is also shown in Fig. 6-(A) by closed circles. The adsorption isotherm of the *cis*-2-butene in Fig. 6-(B) (closed circles) was obtained in the absence of sulfur dioxide.

Effect of the Evacuation Temperature. Following the usual pretreatment of the glass, water vapor was adsorbed at 25 °C under a pressure of 4.6 Torr. Then, the temperature of the glass was raised to a temperature at which the glass was allowed to stand for 1 h; thereafter the system was evacuated for 2 h at the same temperature. With the glass thus treated, the rate of the sulfur dioxide-enhancing isomerization was measured. The data are plotted against the evacuation temperature in Fig. 7.

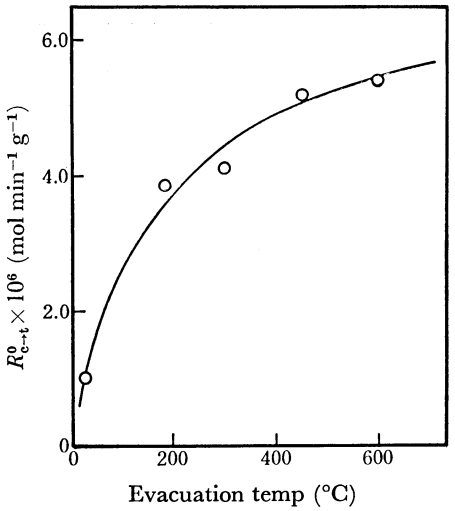

Fig. 7. Effect of evacuation temperature on the rate of the isomerization: reaction at 25 °C; P_{SO_2}=5.0 Torr, $P_{cis\text{-But}}$=90 Torr.

Discussion

The carbonium-ion mechanism, generally accepted for porous glass,[3,4] requires not only the occurrence of the *cis-trans* geometrical isomerization, but also the double-bond migration of normal butenes. The fact that no double-bond migration is observed in the presence of sulfur dioxide suggests that the geometrical isomerization of 2-butenes, enhanced by the addition of sulfur dioxide, proceeds by means of a new mechanism, different from that operative in the absence of sulfur dioxide; sulfur dioxide strongly inhibits the double-bond migration which proceeds on the glass without sulfur dioxide.

D_{SO_2} or D_{But}, the optical density obtained from the data of the individual adsorption of sulfur dioxide or that of *cis*-2-butene, can, in the case of the coadsorption of the two compounds, be used in calculating D_{ctc} by means of equation (i), for the following reasons: (1) The total coverage of the two adsorbates was less than 0.1 under the experimental conditions applied to the data in Fig. 3; (2) a small equilibrium quantity of the charge-transfer complex formed appears in a hexane solution;[5] (3) a much larger extinction coefficient of the complex compared to that of sulfur dioxide has been confirmed.[5]

The two absorption bands at ≈240 and ≈330 nm are seen in Fig. 5; the former was identified as the charge-transfer band of the sulfur dioxide–*cis*-2-butene molecular complex, and the latter, as the enhanced absorption of the sulfur dioxide brought about by the proximity of the π-donating *cis*-2-butene molecule.[2,5] In the following discussion, the D^0_{ctc} at 250 nm, D^0_{ctc} (250), has been adopted as the optical density due to the charge-transfer complex, because it is the most reliable value.

The curves of D^0_{ctc} (250) and the adsorption isotherm in Fig. 6-(A) or those in Fig. 6-(B) indicate a similar dependence on the pressure. Most of the sulfur dioxide or *cis*-2-butene adsorbed on the glass is physically adsorbed; this similar dependence implies that the

complex results from the reaction between the weekly adsorbed sulfur dioxide and *cis*-2-butene.

Role of the Charge-transfer Complex in the Reaction Mechanism. It has been suggested that the selective *cis-trans* isomerization is accompanied by the copolymerization of sulfur dioxide with 2-butenes on the solid surface.[2,6] Since the pressure readings of the reacting gases did not change during the isomerization, the formation of the polymer could not be confirmed in the present work. However, the unknown compound, P_X, giving the tailing spectra in Fig. 4 may possibly be the polysulfone formed from sulfur dioxide and *cis*-2-butene.

In the following discussion, we intend to examine the role of the charge-transfer complex along with the reaction mechanism shown below:[2]

$$SO_2 + \textit{cis}\text{-2-butene} \overset{K}{\rightleftarrows} CTC \quad (1)$$

$$CTC \longrightarrow P_B + P_S \quad (2)$$

$$P_B \longrightarrow P_S + \textit{trans}\text{-2-butene} \quad (3)$$

$$P_B \longrightarrow P_S + \textit{cis}\text{-2-butene} \quad (4)$$

$$P_S \longrightarrow P_B + SO_2 \quad (5)$$

$$P_B + SO_2 \longrightarrow P_S \quad (6)$$

$$P_S + \textit{cis}\text{-2-butene} \longrightarrow P_B \quad (7)$$

$$P_B \longrightarrow \text{stabilized} \quad (8)$$

$$P_S \longrightarrow \text{stabilized} \quad (9)$$

where the mechanism is considered under a low conversion, using 100% *cis*-2-butene as the starting olefin; *CTC* is the charge-transfer complex, and P_B and P_S represent the terminal group of 2-butyl and sulfonyl radical of the active polysulfone respectively.

The steady-state treatment of P_S and P_B with Eq. 1—9 gives the following rate equation by assuming $k_9/2+k_5 \ll k_7[\textit{cis}\text{-2-butene}]$:

$$R^0_{c\to t} = \frac{2k_2k_3k_7[\textit{cis}\text{-2-butene}][CTC]}{k_7k_8[\textit{cis}\text{-2-butene}]+k_9(k_8/2+k_3+k_4+k_6[SO_2])} \quad (ii)$$

where the concentration for the each compound is assigned to that on the surface. Since it has been shown that the equilibrium constant of the formation of the charge-transfer complex is small in a hexane solution ($K=0.075\pm0.082$ l mol^{-1} at 25 °C),[5] a low concentration of *CTC* on the glass can reasonably be assumed, and the Lambert-Beer law holds for the optical density:

$$D^0_{ctc} = \varepsilon[CTC]l \quad (iii)$$

We may then rearrange Eq. ii to Eq. iv to see the effect of the concentration of adsorbed sulfur dioxide:

$$\frac{D^0_{ctc}}{R^0_{c\to t}} = A + B[SO_2] \quad (iv)$$

where

$$A = \frac{\varepsilon l}{2k_2k_3}\left\{k_8+\frac{k_9(k_8/2+k_3+k_4)}{k_7[\textit{cis}\text{-2-butene}]}\right\}$$

$$B = \frac{\varepsilon l}{2k_2k_3}\left\{\frac{k_6k_9}{k_7[\textit{cis}\text{-2-butene}]}\right\}.$$

Using the data of $R^0_{c\to t}$ in Fig. 1 and those of D^0_{ctc} (250) and V_{SO_2} in Fig. 6 at the *cis*-2-butene pressure of 6.2 Torr, where the concentration of the adsorbed *cis*-2-butene is assumed to be constant because of the low total coverage of the adsorbed compounds ($\theta<0.1$),

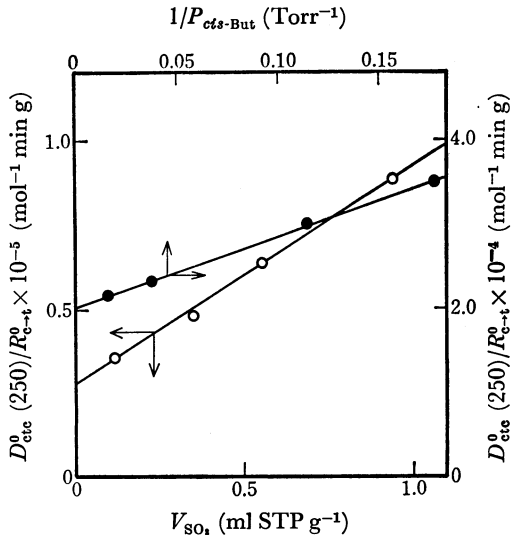

Fig. 8. Plot of $(D^0_{ctc}(250)/R^0_{c\to t})$ against the amount of sulfur dioxide adsorbed (○), or that against the inverse of *cis*-2-butene pressure (●).

$D^0_{ctc}(250)/R^0_{c\to t}$ is plotted against V_{SO_2} in Fig. 8 (open circles). A reasonably good linear relation is obtained between the variables.

Assuming that the *cis*-2-butene in the propagation step (7) is chemically adsorbed on the active site of the glass and that the adsorption isotherm can be represented by a Langmuir-type equation such as:

$$[\textit{cis}\text{-2-butene}] = \frac{b(P_{\textit{cis}\text{-But}})}{1+b(P_{\textit{cis}\text{-But}})} \quad (v)$$

we may rearrange Eq. ii to Eq. vi:

$$\frac{D^0_{ctc}}{R^0_{t\to c}} = C + D(P_{\textit{cis}\text{-But}})^{-1} \quad (vi)$$

where

$$C = \frac{\varepsilon l}{2k_2k_3}\left\{k_8+\frac{k_9}{k_7}\left(\frac{k_8}{2}+k_3+k_4+k_6[SO_2]\right)\right\}$$

$$D = \frac{\varepsilon lk_9}{2k_2k_3k_7b}\left(\frac{k_8}{2}+k_3+k_4+k_6[SO_2]\right).$$

$D^0_{ctc}(250)/R^0_{c\to t}$, calculated from the data in Fig. 6 and Fig. 2 at a fixed pressure of sulfur dioxide (=4.9 Torr), is plotted against $1/P_{\textit{cis}\text{-But}}$ in Fig. 8 (closed circles); the plot confirms the theoretically expected linear relation of the plot.

Consequently, the results in Fig. 8 confirm the previously predicted hypothesis[2] that the charge-transfer complex initiates the reaction by Process (2).

The Nature of the Active Site on the Porous Vycor Glass. Figure 7 shows that the catalytic activity of the glass increases with a rise in the evacuation temperature. In contrast to this result, if sulfur dioxide is absent, the activity of the glass decreases with the evacuation temperature from 400 to 700 °C;[7] this is consistent with the results reported by Blomfield and Little.[8] It has been suggested that the alumina contained in the porous Vycor glass is responsible for the catalytic activity of the glass.[3,4] West, Haller, and Burwell also suspected that most of the reported reactions over silica gel occur at impurity sites, most likely Al^{3+}.[9] In the studies of the isomerization of normal butenes over

silica–alumina, it has been found that the rate of reaction decreases as the concentration of hydroxyl groups on the catalyst is decreased by a rise in the evacuation temperature.[10,11] On the contrary, on an alumina catalyst, the reaction rate is inversely related to the surface density of hydroxyl groups,[10–12] suggesting that the active sites involve the exposure of aluminum ions, creating dual acid-base sites[12] when hydroxyl groups are removed. Hence, if the silica–alumina site on the porous Vycor glass is much more active than the exposed aluminum ion site for the normal butene isomerization in the absence of sulfur dioxide, the opposite dependences of the isomerization rates on the evacuation temperature in the presence and in the absence of sulfur dioxide can be explained by considering that the reaction in the absence of sulfur dioxide occurs on the silica–alumina-type site, while the one in the presence of sulfur dioxide proceeds on similar sites over an alumina catalyst.[11,12] It is probable that sulfur dioxide strongly adsorbs on the silica–alumina site and, accordingly, poisons the double-bond migration of the butenes. If the sulfur dioxide–*cis*-2-butene molecular complex approached the exposed aluminum ions, it would be polarized by the strong electrostatic field surrounding these cations toward the radical-ion structure $\dot{S}O_2CH(CH_3)\overset{+}{C}H(CH_3)$, and this could readily initiate the polysulfone formation and the accompaning geometrical isomerization.

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