Free Radical Mechanism in Olefin Isomerization

Isomerization of (Z)-But-2-ene and (Z)- $[1,2^{-2}H_2]$ Ethylene over Siloxene

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Isomerization of (Z)-but-2-ene and (Z)- $[1,2-^{2}H_{2}]$ ethylene over siloxene has been studied. The isomerization of (Z)-but-2-ene gives (E)-but-2-ene as sole product and the double bond migration reaction does not proceed. The isomerization of (Z)- $[1,2-^{2}H_{2}]$ ethylene gives (E)- $[1,2-^{2}H_{2}]$ ethylene and scrambling of deuterium atoms does not occur. Both the radical species on siloxene and the butene isomerization activity sharply increase with the heat treatment temperature of siloxene. Free radical mechanisms for isomerizations are proposed.

The isomerizations of alkenes have been the subject of many investigations and various mechanisms for the reactions have been proposed.¹⁻²³ In the majority of the cases, the double bond migration and the structural interconversion occur simultaneously. For example, the isomerization of (Z)-but-2-ene gives both but-1-ene and (E)-but-2-ene.

In a previous communication,²⁴ the present authors and Keii have reported that siloxene $[(Si_6O_3H_6)_n]$ has a catalytic activity for the structural isomerization of butenes, but no activity for double bond migration and we suggested a mechanism involving a free radical intermediate. In this work, in order to clarify the free radical nature of the isomerization, the isomerization of (Z)-but-2-ene has been studied in some detail and the isomerization of (Z)-[1,2-²H₂]ethylene has also been studied.

EXPERIMENTAL

MATERIALS

Siloxene was prepared by the method described by Kautsky.²⁵ Calcium silicide (3 g) was added to a mixture of 360 cm^3 n-propanol, 62 cm^3 water and 11 cm^3 concentrated hydrochloric acid at 273 K. The mixture was continuously agitated in the dark under a helium atmosphere. After a week, the product was filtered under helium and washed with n-propanol and then with diethyl ether at 273 K.

(Z)-but-2-ene (Takachiho Kogyo, 99.2 %) and (Z)- $[1,2^{-2}H_2]$ ethylene (Merck, 98 % D atomic purity) were further purified by vacuum distillation prior to use.

PROCEDURES

Isomerization was carried out using two types of reaction apparatus. In the first method, the reaction was carried out in a static system in a 35 cm³ glass vessel. The products were analysed after the reaction. In the second method, a gas-circulation system with 170 cm³ dead volume was used. The catalyst was packed in Pyrex tubing and the products were periodically withdrawn and analysed. Butenes were analysed by gas chromatography. The compositions of the deutero-ethylenes were determined by an infrared spectroscopic method using a Hitachi-295 spectrophotometer. The bands at 842 and 987 cm⁻¹ were used

for the determination of (Z)- and (E)- $[1,2-^{2}H_{2}]$ ethylene, respectively. For e.s.r. measurements, the sample, placed in a 4 mm i.d. e.s.r. tube, was evacuated under vacuum for 3 h at various temperatures. The measurements were carried out at room temperature with a JEOL spectrometer (JES-PE-IX) with a 100 kHz field modulation. Radical concentration was determined by comparison of the doubly integrated intensities of the observed spectra with those of a benzene solution of 1,1-diphenyl-2-picryl hydrazyl.

RESULTS AND DISCUSSION

EFFECT OF HEAT TREATMENT ON SILOXENE STRUCTURE

It has been reported that siloxene in a closed vessel was stable up to 413 K and decomposed to give gaseous products (H₂, SiH₄, *etc.*) at higher temperature.²⁶ Here, the thermal stability of siloxene was examined by i.r. and e.s.r. spectroscopy. Siloxene was evacuated at various temperatures for 3 h. The siloxene prepared had a whitish grey colour. The colour changed to light grey on treatment at 473 K, to yellowish green at 523 K and to brown at 773 K.

The B.E.T. surface area of siloxene was $792 \text{ m}^2 \text{ g}^{-1}$ and it was decreased slightly to 582 and 548 m² g⁻¹ by treatment at 573 and 673 K. A drastic decrease (to 147 m² g⁻¹) was observed on treatment at 773 K.

The infrared spectrum of siloxene shows two bands due to Si—H stretching at 2120 and 2250 cm⁻¹. The first band was decreased slightly in intensity by heat treatment at 473 K and disappeared completely at 773 K, while the second band was stable at 773 K. The intensity of the 2120 cm⁻¹ band was not recovered by contacting the sample treated at 473 or 773 K with hydrogen at that temperature for 10 min.



FIG. 1.—Change in the concentration of the radical species on siloxene and the rate of (Z)-but-2-ene isomerization with heat treatment temperature of siloxene.

Siloxene showed an e.s.r. spectrum of g = 2.004 with a line width of 0.62 mT. The spin density of the solid increased drastically with the temperature of the heattreatment *in vacuo*, as shown in fig. 1. The line shape or g-value of the spectra did not depend on the evacuation temperature, showing that the radical species were the same, irrespective of the heat-treatment temperature. The above results suggest that siloxene loses some Si—H bonds due to radical species formation with structural change during heat-treatment in vacuum.

ISOMERIZATION OF (Z)-BUT-2-ENE

Typical time courses of (Z)-but-2-ene isomerization are shown in fig. 2 and 3. Siloxene was heated *in vacuo* at 773 K for 3 h and the isomerization was carried out using the gas circulation system. Fig. 2 shows the time courses at 478 and 453 K and fig. 3 shows the effect of pressure at 478 K. In each case, (E)-but-2-ene is the only product and but-1-ene is not formed at all, in accordance with the previous communication.²⁴ A slight pressure drop was observed, suggesting polymerization of the butenes on the surface. The coverage of polymerized material over the siloxene surface is 79 and 40 % at 13.9 and 5.44 kN m⁻², respectively, at 478 K after a reaction time of 1800 s. The molecular cross-section area of butene is $40.6 \text{ Å}^{2.27}$ The active sites for isomerization seem to be poisoned by the polymerization and the rate decreases gradually with reaction time.

The effect of the heat-treatment temperature of siloxene on the rate of the isomerization is given in fig. 1, which shows that the rate increases exponentially with the heat-treatment temperature, as does the concentration of the radical species. Thus,



FIG. 2.—Pressure against time plots for (Z)-but-2-ene isomerization. Effect of reaction temperature ○, 478 K; △, 453 K. —, total pressure; ---, (E)-but-2-ene pressure; ---, (Z)-but-2-ene pressure.

the rate is approximately proportional to the concentration of the radical species. However, the e.s.r. spectrum of siloxene shows little change upon contact with butenes, indicating that only a small portion of radical sites are occupied by adsorbed molecules.



FIG. 3.—Pressure against time plots for (Z)-but-2-ene isomerization. Effect of initial pressure at 478 K with 0.1 g catalyst. \bigcirc , 13.9; \times , 11.19; \triangle , 5.44 kN m⁻². —, total pressure; ---, (E)-but-2-ene pressure; ---, (Z)but-2-ene pressure.

TABLE 1.—PRODUCT DISTRIBUTION FOR ISOMERIZATION OF (Z)-[1,2-²H₂]ETHYLENE OVER SILOXENE

activation	reaction	weight of	(Z)-C ₂ H ₂ D ₂ pressure	product/%	
temp./K	temp./K	catalyst/mg	/kN m ⁻²	(Z)-C ₂ H ₂ D ₂	(E)-C ₂ H ₂ D ₂
373	353	53	2.91	96.8	3.2
473	354	67	2.16	96.8	3.2
473	463	68	3.21	88.4	11.6
773	313	56	2.91	74.3	25.7
773	353	50	2.83	60.1	39.9
773	464	43	3.83	53.7	46.3

Reaction time: 10 min.

ISOMERIZATION OF (Z)-[1,2-²H₂]ETHYLENE

The isomerization of (Z)-[1,2-²H₂]ethylene was carried out using the static reactor with a dead volume of 35 cm³. Siloxene was treated *in vacuo* at 373-773 K and (Z)-[1,2-²H₂]ethylene was introduced. After 10 min, the products were determined by infrared spectroscopy. The results are summarized in table 1. The starting (Z)-[1,2-²H₂]ethylene contained 3.2 % of (E)-[1,2-²H₂]ethylene. The reaction did not proceed at 353 K on the samples treated at 373 or 473 K. The reaction did proceed at 463 K for the sample treated at 473 K. For the samples treated at 773 K, the reaction occurred even at 313 K. In every case, (E)-[1,2-²H₂]ethylene was the only product and $[1,1-^{2}H_{2}]$ ethylene, $[^{1}H_{2}]$ ethylene and $[^{3}H_{2}]$ ethylene were not formed at all. Thus the isomerization proceeds without scrambling of H and D atoms in the ethylene molecules.

The activity increases with increasing pretreatment temperature of siloxene as for (Z)-but-2-ene isomerization. This suggests that the same mechanism is operative for both isomerizations.

The kinetics of (Z)-[1,2-²H₂]ethylene were examined. The total pressure of the gas phase is constant at all times. The change in the gas-phase composition can be expressed by the following equation :

$$\ln \frac{x_0 - x_e}{x - x_e} = kt,$$
$$k = \frac{w RT r}{PV(1 - x_e)},$$

where x_0 , x and x_e (= 0.5)²⁸ are the molar fraction of (Z)-[1,2-²H₂]ethylene at time 0, t and equilibrium, respectively. P, V, T and w are the total pressure, the volume of the system, the reaction temperature and the weight of the catalyst. **R** is the gas constant and r is the rate of the (Z)-(E) interconversion. The rate (r) was calculated from the apparent rate, k, obtained experimentally and found to be zero order with respect to ethylene pressure. The temperature dependence of the rate (r) gave an apparent activation energy of 74.5 kJ mol⁻¹.

MECHANISM OF BUTENE ISOMERIZATION

Many mechanisms for butene isomerization have been proposed so far.¹⁻²³ Most of them assume a common intermediate for double-bond shift and (Z)-(E) interconversion and cannot explain the exclusive enhancement of the latter reaction. For example, the isomerization of (Z)-but-2-ene in the presence of Brönsted acid sites could be explained by a carbenium ion mechanism.



Several systems which could catalyse the structural isomerization without inducing double-bond shift have been found and a mechanism for the isomerization is suggested. (a) Kemball et al.¹³ and Foster and Cvetanovic ¹² suggested a secondary butyl carbonium ion intermediate for the isomerization by tin oxide and sulphonic acid, respectively. (b) Davie et al.¹⁴ proposed that the isomerization proceeded by a disproportionation type mechanism over molybdenum hexacarbonyl supported on alumina. (c) Guisnet et al.¹⁵ proposed that the isomerization over sodium exchanged alumina proceeded via a mechanism with an allylic C—H bond-breaking step occurring on Lewis acid-base pair sites. (d) Rooney and coworkers 16-18 proposed that the intermediate was σ -bonded vinyl adsorbed on oxide ions for the isomerization over gallium oxide. A similar mechanism was proposed by Sakai and Hattori¹⁹ for butene isomerization over aluminium phosphate evacuated at 873 K. (e) A free radical mechanism was first suggested for isomerization over pyrolytic carbon.²⁰ The isomerization of alkenes via the free radical intermediates are well established for homogeneous catalysis in the gas phase.²⁹⁻³³ Later, Otsuka et al.²¹⁻²³ suggested that isomerization induced by adsorbed SO_2 or NO_2 was via a free radical mechanism.

Mechanism (a) has difficulty in explaining the complete absence of the double-bond shift, since the secondary butyl carbonium ion could easily form but-1-ene. Mechanism (b) is not applicable to the present system, since siloxene has no catalytic activity for alkene disproportionation. Mechanism (c) is also rejected, since the mechanism does not explain (Z)-(E) conversion of (Z)- $[1,2-^{2}H_{2}]$ ethylene.

Mechanisms (d) and (e) can explain both (Z)-(E) isomerizations of (Z)-but-2-ene and (Z)-[1,2-²H₂]ethylene, though the former mechanism has difficulty in explaining the absence of H-D scrambling in the ethylene isomerization.

The fact that the rate of butene isomerization increases in the same manner as both the radical concentration on the surface and the temperature of heat-treatment suggests a free radical mechanism for the isomerization over siloxene. The occurrence of styrene polymerization on the surface supports this view.²⁴

Thus, we conclude that the isomerizations of (Z)-but-2-ene and (Z)- $[1,2-{}^{2}H_{2}]$ -ethylene proceed via a free radical intermediate, as follows:





where -S-denotes the surface radical species.

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