JOURNAL OF CATALYSIS 55, 263–271 (1978)

Cis–trans Isomerization of *cis*-2-Butene Catalyzed by Nitrogen Dioxide Adsorbed on Porous Silica Glass

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Received October 7, 1977; revised July 24, 1978

Nitrogen dioxide adsorbed on porous Vycor glass has been found to catalyse selectively the *cis–trans* isomerization of *cis*-2-butene at room temperature. The presence of NO_2 radical on the glass adsorbing the nitrogen dioxide gas has been confirmed by esr observation. It has been found by ir spectroscopic measurements that in the presence of the adsorbed nitrogen dioxide the olefinic =C–H stretching vibration band of the adsorbed butene molecules disappears. The isomerization apparently consists of two reactions; one proceeds with a high but unsteady rate, and the other with a low and steady rate. The latter is first order in the amount of adsorbed nitrogen dioxide and half order in the pressure of *cis*-2-butene, with an apparent activation energy of 11.3 kcal mol^{-1}. The rate-determining step has been proposed to be the addition of NO_2 radical to the double bond of the butene, followed by rotation about the central C–C bond. The kinetic results of the unsteady reaction have been discussed in relation to the steady reaction.

INTRODUCTION

In preliminary experiments, the present authors found that the catalytic isomerization of butenes at room temperature could be induced by various adsorbents with adsorbed nitrogen dioxide (*1*), as well as materials with adsorbed sulfur dioxide (*2*) or carbon dioxide (*3*). Among the adsorbents tested, porous Vycor glass was a unique adsorbent in that only the *cis–trans* geometrical isomerization of 2-butenes was catalyzed. This kind of selectivity appears with the various catalysts adsorbing sulfur dioxide (*2*) and with siloxene (*4*), which has been interpreted by adapting a radical mechanism for the isomerization. It has been shown that the selective geometrical isomerization of olefins in homogeneous system is catalyzed by NO_2 (*5–7*) and other free radicals (*8–11*).

We here report the results of both kinetic and ir or esr spectroscopic studies on the catalytic isomerization of *cis*-2-butene with a nitrogen dioxide–porous Vycor glass system. From the point of view of air pollution chemistry, the investigation of the reaction in an olefin–NO_2-solid system is worthwhile in considering the chemical role which dusts would play in smog formation.

EXPERIMENTAL METHODS

Materials. A porous Vycor glass (Corning No. 7930) plate with a thickness of 0.8 to 1.0 mm or a rod with a diameter of 3.5 mm was used. The glass samples were washed with water for 3 hr in a Soxhlet

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0021-9517/78/0553-0263$02.00/0

extractor and calcined in air at 750°C for 5 hr. Their BET surface area determined by nitrogen adsorption was 150 m^2 g^{-1}.

Nitrogen dioxide was obtained by the reaction between nitrogen monoxide and oxygen in a grease- and mercury-free apparatus, and stored in the dark in a glass bulb together with oxygen. Immediately before its use, nitrogen dioxide was degassed and distilled *in vacuo*. Thus nitrogen dioxide free from dinitrogen trioxide was obtained.

Nitrogen monoxide, *trans*-2-butene, and 1-butene (guaranteed reagent grade from Takachiho Kagaku Kogyo Co.), oxygen gas (commercial grade), and *cis*-2-butene (research grade from Phillips Petroleum Co.) were purified by degassing, distillation and/or passing through a cold trap (77 or 195 K) in the usual manner. The purity of the *cis*-2-butene as determined by gas chromatography was more than 99.9% and the *trans*-2-butene and 1-butene were not less than 99.0%.

Apparatus. The isomerization of butenes was carried out in a mercury- and grease-free, closed, gas-circulating, glass apparatus in which a vacuum of 10^{-6} Torr was achieved. The reactor attached to the gas-circulating part has the form of a coaxial tube, to the bottom of which a rectangular quartz cell (10 × 10 × 40 mm) is fused. The reactor is separable from the gas-circulating part of the apparatus in order to make the spectroscopic investigation of the catalysts possible. The volume of the reaction system is 220 ml.

Procedures. The porous Vycor glass sample was settled in the rectangular part of the reactor. Prior to each experimental run, the glass sample was calcined in a stream of dry oxygen for 1 hr at 650°C, degassed under a vacuum of 10^{-5} Torr for 2 hr at the same temperature, and cooled to room temperature in a helium gas medium. After the helium gas was evacuated, nitrogen dioxide was adsorbed onto the glass at an appropriate pressure for 1 hr and evacuated 45 min up to 10^{-5} Torr pressure. The amount of the nitrogen dioxide adsorbed was determined by subtracting the amount evacuated from that introduced. Nitrogen dioxide is in the following equilibrium,

$$N_2O_4 \rightleftarrows 2\ NO_2, \qquad (1)$$

where the equilibrium constant is 86.34 Torr at 25°C in the gas phase (*12*). The amount of nitrogen dioxide on the surface is expressed as moles of NO_2 per gram of glass, denoted by $\{NO_2\}$ hereafter.

The isomerization of *cis*-2-butene was initiated by introducing the butene at an appropriate pressure onto the glass. The reaction products were periodically analyzed by gas chromatography by taking a small fraction of the gas in the reaction system. All kinetic data were obtained when the *cis*-2-butene conversion was less than 15%. The desorption of the adsorbed nitrogen dioxide due to introducing the butene gas was hardly observable.

Spectroscopic measurements. The ir absorption spectra of the species adsorbed on the fivefold glass plates (5.0 mm thickness) were measured with a JASCO IR-1 spectrometer.

Electron spin resonance absorption spectra for the glass rod sealed in a quartz tube with a 5.0 mm outer diameter were obtained with a JES 3BS-X, an X band spectrometer. The g values were determined by means of manganese divalent cation markers.

RESULTS

Kinetics. In Fig. 1, the amounts of *trans*-2- and 1-butenes isomerized from *cis*-2-butene are shown as a function of reaction time. Without adsorbed nitrogen dioxide, *trans*-2-butene and 1-butene are formed at the very low rates of 1.54×10^{-9} and 2.57×10^{-9} mol sec^{-1} g^{-1}, respectively, which are comparable to the results obtained for the glass degassed at low temperature (*13*). In the presence of the

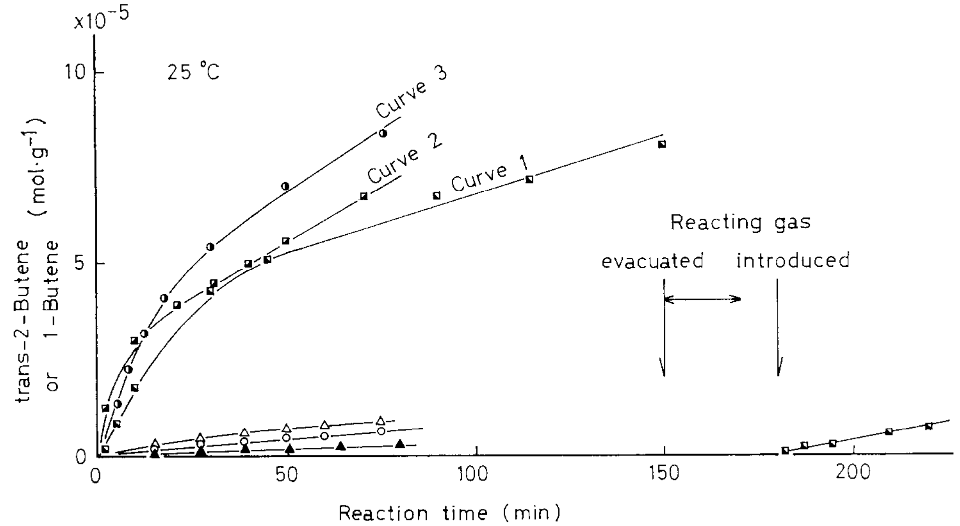


FIG. 1. The course of the isomerization of *cis*-2-butene to *trans*-2-butene, with $\{NO_2\} = 0$ mol g^{-1} on the rod (○), 9.3×10^{-6} mol g^{-1} on the plate (◩), 27.7×10^{-6} mol g^{-1} on the plate (◪), 36.2×10^{-6} mol g^{-1} on the rod (◑), and to 1-butene, with $\{NO_2\} = 0$ mol g^{-1} on the rod (△), and 10.2×10^{-6} mol g^{-1} on the plate (▲), at 25°C.

adsorbed nitrogen dioxide, $\{NO_2\} = 10 \times 10^{-6}$ mol g^{-1}, the formation of the *trans* isomer of 2-butene is considerably accelerated, while that of 1-butene is remarkably retarded. Nitrogen dioxide adsorbed in the amount of $\{NO_2\} = 20 \times 10^{-6}$ mol g^{-1} is effective enough to suppress 1-butene formation. This paper presents the kinetics of the *cis–trans* isomerization accelerated by the adsorbed nitrogen dioxide.

The isomerization is considered to be separated into an earlier stage with a high rate and a later stage with a low rate. After 150 min of time for the reaction shown by Curve 1 in Fig. 1, the reacting gas was evacuated for 20 min, then the gas was reintroduced at 180 min at the same pressure as before. The reaction proceeded steadily and 80% of the previous steady rate was recovered. This indicates that the reaction in the earlier stage is diminished as the reaction proceeds, while the reaction in the later stage occurs steadily. As the amount of adsorbed nitrogen dioxide increases, the initial rate, i.e., the slope at the initial stage of the reaction curves, increases as shown by Curves 1 and 2. The further increase of $\{NO_2\}$ results in a decrease of the initial rate (Curve 3). On the contrary, the rate at the later stage shows a continuous increase (Curves 1, 2, and 3). In Fig. 2, the dependence of both the initial rate, r_i, and of the steady rate, r_s, on $\{NO_2\}$ are displayed. The latter is proportional to $\{NO_2\}$. The rate, r_i, is

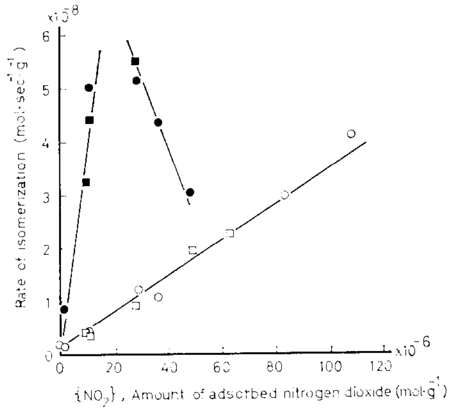


FIG. 2. The dependence on NO_2 of the initial rates [(●) on the rod and (■) on the plate] and the steady rates [(○) on the rod and (□) on the plate], observed at pressures of *cis*-2-butene, 43 to 53 Torr, at 25°C.

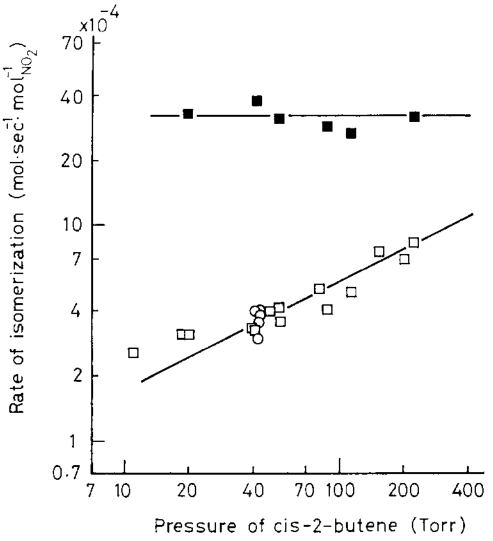


FIG. 3. The dependences on the pressure of *cis*-2-butene, for the initial rates at $\{NO_2\} = 9 \times 10^{-6}$ mol g^{-1} on the plate (■) and for the steady rates with the various values of NO_2 [on the plate (□) and on the rod (○)], at 25°C.

also proportional to $\{NO_2\}$, however if $\{NO_2\}$ exceeds 20×10^{-6} mol g^{-1}, r_i decreases. Therefore, the reaction having a steady rate seems to occur even at the earlier stage of the reaction, and to proceed steadily throughout the reaction time. Thus the net rate of the initial reaction, r_{in}, is determined as $r_{in} = r_i - r_s$.

The rate r_{in} has a zero order dependence on *cis*-2-butene pressure, while r_s is half order, as shown in Fig. 3. The experimental rate equations were determined as follows;

$$r_{in} = k_{in} \cdot f(\{NO_2\}) \cdot P^{0.0}, \qquad (2)$$

$$r_s = k_s \cdot (\{NO_2\})^{1.0} \cdot P^{0.5}, \qquad (3)$$

where P is the pressure of *cis*-2-butene, k_{in} and k_s are rate constants, and f means a function describing the dependence of the rate on $\{NO_2\}$.

The Arrhenius plots of k_{in} and k_s, shown in Fig. 4, give activation energies of 5.5 and 11.3 kcal mole^{-1} for the initial and steady reactions, respectively.

Infrared absorption spectra. The ir absorption spectra of the adsorbed nitrogen dioxide are shown in Figs. 5 and 6. As the equilibrium pressure of nitrogen dioxide increases, a band at 2938 cm^{-1} appears first, then two strong bands, 3100 and 2963 cm^{-1}, and a weak band, 2893 cm^{-1} grow. The latter absorption is eventually covered with a strong band. Evacuation of the gas phase for 1 min gives no appreciable change in the bands as shown in spectrum d in Fig. 5. The two strong bands at 3100 and 2963 cm^{-1} are identified with the $\nu_1 + \nu_9$ and $\nu_5 + \nu_{11}$ modes of N_2O_4 (*14*) and the weak band at 2893 cm^{-1} with the $\nu_1 + \nu_3$ of NO_2 (*14*), which show 7, 9, and 14 cm^{-1} red shifts, compared to the corresponding bands, 3107, 2972, and 2907 cm^{-1}, observed for gaseous nitrogen dioxide at a pressure 32 Torr and 24°C. Gaseous nitrogen dioxide actually contains 23.3% N_2O_4, and the NO_2 band at 2907 cm^{-1} is 3.7 times as intense as the N_2O_4 bands, 3107 and 2972 cm^{-1}. This indicates that the main fraction of the adsorbed species is N_2O_4.

If the adsorbed nitrogen dioxide is evacuated for a long time at room temperature, the intensity of the three bands, 3100, 2963, and 2893 cm^{-1} becomes smaller. It is concluded that the nitrogen dioxide species are physically adsorbed on the surface. On

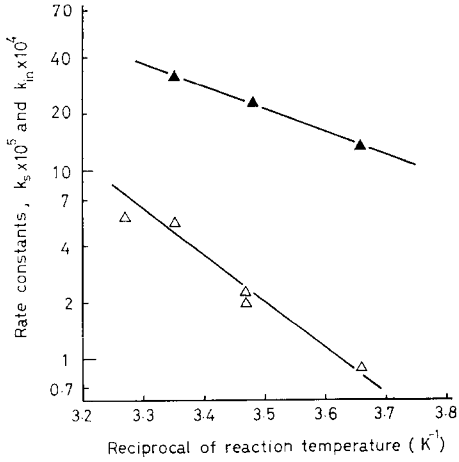


FIG. 4. The Arrhenius plots of the rate constants, k_{in} (▲) mol sec^{-1} mol$_{NO_2}$$^{-1}$ Torr$^{-\frac{1}{2}}$, and k_s (△) mol sec^{-1} mol$_{NO_2}$$^{-1}$.

the other hand, the band at 2938 cm^{-1} may correspond to a chemically adsorbed species, because its intensity seems unaffected even after degassing at 100 to 120°C (shown by spectrum f in Fig. 6). It is expected that the nitrite ion or a nitrato complex would be formed (*15*). Other bands, such as the antisymmetric stretching vibration observed on V_2O_5 at 1632 cm^{-1} (*16*), cannot be observed because silica strongly absorbs ir radiation of less than 2000 cm^{-1}.

The ir spectra of the adsorbed butenes were examined also. Spectrum j in Fig. 6 is from 0.002 coverage of *cis*-2-butene, which is different from spectrum for the adsorbed *trans*-2-butene. It remains unchanged even after 80 min. The shape of the spectrum is also unchanged on increasing the coverage to 0.03 or decreasing it by degassing. It is concluded that *cis*-2-butene is weakly bound to the glass surface and is hardly isomerized. The 3027 cm^{-1} band is identified with the olefinic C–H stretching vibration ν(=C–H).

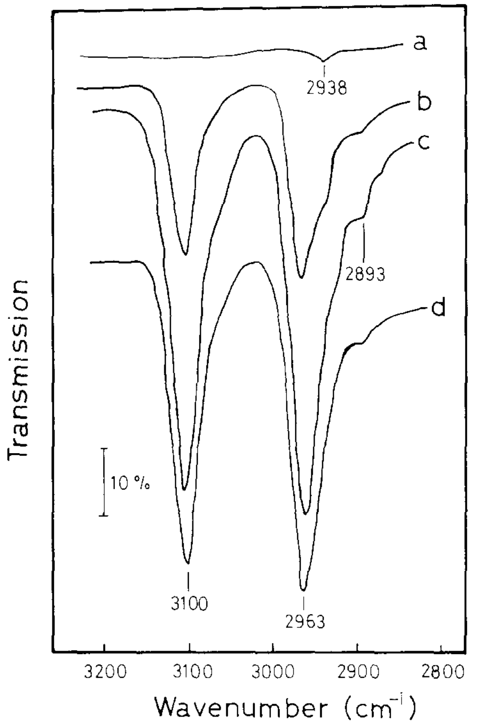


FIG. 5. The ir absorption spectra of nitrogen dioxide adsorbed on porous Vycor glass at various pressures of nitrogen dioxide, at 25°C: (a) 0.9 Torr; (b) 7.0 Torr; (c) 18.8 Torr; (d) degassing c for 1 min.

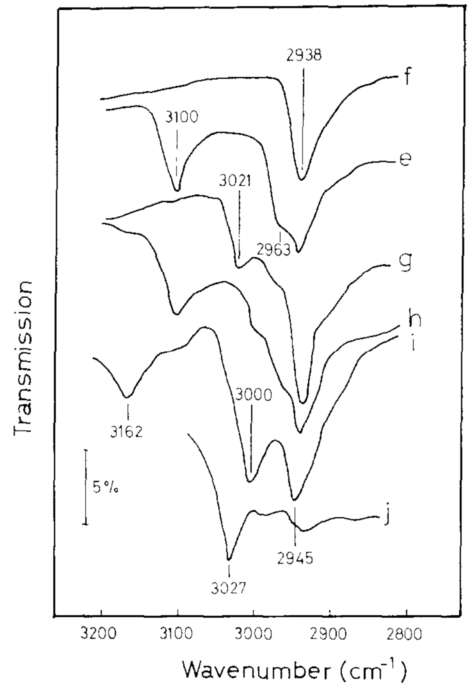


FIG. 6. The ir absorption spectra of nitrogen dioxide and *cis*-2-butene adsorbed on porous Vycor glass at 25°C: (e) with $\{NO_2\}$ = 35.3 × 10^{-6} mol g^{-1}; (f) 18.3 × 10^{-6} mol g^{-1}, degassed for 5 min at 100 to 120°C in addition to the standard adsorption procedure; (g) added *cis*-2-butene of coverage 0.002 on f; (h) added *cis*-2-butene of coverage 0.002 on e; (i) 17 hr after the addition of *cis*-2-butene of coverage 0.007 on e; (j) *cis*-2-butene of coverage 0.002.

The introduction of *cis*-2-butene onto the surface, which already adsorbed NO_2 and has the band at 2938 cm^{-1}, changes spectrum f into spectrum g in Fig. 6. These spectra seem to be a superposition of spectra, f and j. The 3021 cm^{-1} ν(=C–H) band is observed in spectrum g with a 6 cm^{-1} red shift.

In the presence of the physically adsorbed nitrogen dioxide species, spectrum h instead of e is observed after introducing *cis*-2-butene. The ν(=C–H) band disappears. Seventeen hours after the introduction of

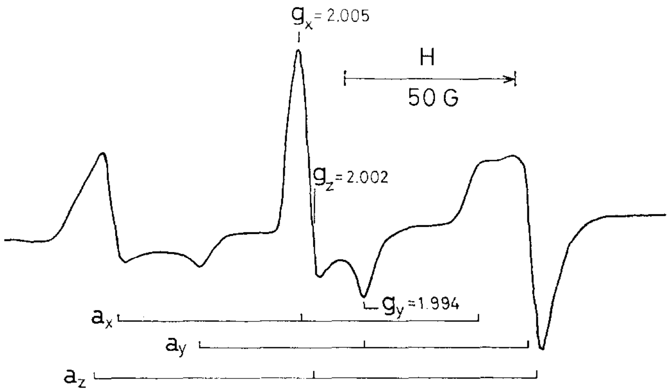


FIG. 7. The esr absorption spectrum of NO_2 radical adsorbed on porous Vycor glass with $\{NO_2\} = 32.1 \times 10^{-6}$ mol g^{-1}, observed at 77 K.

cis-2-butene, spectrum h has been deformed into a spectrum i with absorption bands at 3162, 3000 and 2945 cm^{-1}.

Electron spin resonance measurements. Figure 7 shows the esr spectrum observed for NO_2 radical at 77 K on porous Vycor glass with $\{NO_2\} = 32 \times 10^{-6}$ mol g^{-1} of adsorbed nitrogen dioxide. The g values and hyperfine coupling constants correspond to $g_x = 2.005$, $g_y = 1.994$, $g_z = 2.002$, and $|a_x| = 51.8$ G, $|a_y| = 47.9$ G, $|a_z| = 63.7$ G, respectively. The results were compared with the ample data for NO_2 radicals in various states (*17*), especially in the adsorbed states on MgO (*18*), silica gel (*19*), or zeolites (*20*). Using the above data and the methods described in detail in the references (*17*, *21–23*), we estimate the $4a_1$ molecular orbital of NO_2 is occupied by an unpaired electron. Following the same techniques of orbital estimation and the spectral data for the gaseous NO_2 molecule (*24*), we estimate 10% of the unpaired electron must be shared by the surface. Furthermore, the molecular orbital calculation (*25*) suggests that the electron is localized mainly in nitrogen hybrid sp^2 and oxygen p_z orbitals, similar to the gaseous NO_2. It can be thus inferred that the radical characteristics of NO_2 molecules adsorbed on porous Vycor glass are not much different from those in the gas phase. At 293 K g_x and g_z are unresolved in the spectrum, suggesting that NO_2 molecules interact with hydroxyl groups of the surface, like those adsorbed on silica gel (*19*). At 77 K the esr absorption intensity observed for adsorbed NO_2 radical is proportional to $\{NO_2\}$ within the range of $2–100 \times 10^{-6}$ mol g^{-1}.

If only the ir absorption band of 2938 cm^{-1} is observed after evacuating nitrogen dioxide from the surface at 100 to 120°C, then no esr absorption is observed. This supports the identification of the 2938 cm^{-1} band as corresponding to a diamagnetic nitrite structure for adsorbed NO_2.

Four hours after introducing *cis*-2-butene onto glass which has adsorbed a rather large amount of nitrogen dioxide, $\{NO_2\} = 120 \times 10^{-6}$ mol g^{-1}, an esr spectrum with a g value of 2.002 and splitting constant of 32 G, as shown in Fig. 8, is observed at room temperature. The spectrum is too poorly resolved to identify accurately the perpendicular g value and splitting constant, but its shape is similar to that of a nitroxide such as observed for α-methylstyrene with NO_2 in the liquid phase (*26*) which has a $g_{//} = 2.0023$, $g_{\perp} = 2.007$, $a_{//} = 34.6$ G, and $a_{\perp} = 4.8$ G.

DISCUSSION

The catalysis of the isomerization of *cis*-2-butene by adsorbed dioxide proceeds independently of the shape and surface properties of Vycor glass, because whether plate or rod adsorbent is used, the rate of isomerization shows a common dependence on the amount of adsorbed nitrogen dioxide as shown in Fig. 2.

It is a prominent fact that adsorbed nitrogen dioxide greatly enhances the *cis–trans* geometrical isomerization, whereas it poisons the double-bond-migrating (dbm) isomerization. Since the catalytic activity of the porous Vycor glass for butene isomerizations is attributed to the presence of acid sites (*13*, *27*, *28*), both the geometrical and dbm isomerizations should be affected in the same way as far as a common reaction intermediate, such as a carbenium ion, is concerned. Therefore, the selective enhancement of the reaction rate for the *cis–trans* isomerization cannot be interpreted by a mechanism involving a solid acid catalyst. This reaction must be explained by the presence of NO_2 radical catalysis.

It has been reported that the *cis–trans* isomerization of butenes is appreciably catalyzed by NO_2 in the gas phase, and its rate is proportional to the concentrations of NO_2 and *cis*-2-butenes (*5*). If this occurs in the adsorbed state, the rate must be proportional to their concentrations on the surface. This is supported by the fact that the amount of *cis*-2-butene adsorbed onto the glass is proportional to a 0.4 to 0.6 power function of its pressure in the range of 20 to 150 Torr and the esr absorption intensity of NO_2 radical on the glass adsorbing nitrogen dioxide is proportional to $\{NO_2\}$. The apparent activation energy for k_s, the rate constant of the steady reaction, is 11.3 kcal mol^{-1}. The heat of adsorption of *cis*-2-butene to the glass was determined to be 8.4 kcal mol^{-1}. Therefore, the net activation energy for the radical process in the adsorbed phase is calculated to be 15.5 kcal mol^{-1}, which corresponds reasonably to the value obtained in the gas phase, 12.1 kcal mol^{-1} (*5*).

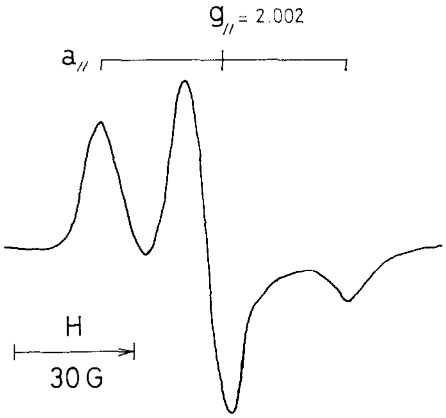
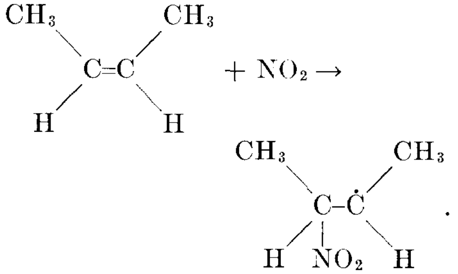


FIG. 8. The esr absorption spectrum observed at room temperature 4 hr after the introduction of *cis*-2-butene onto porous Vycor glass with $\{NO_2\} = 120 \times 10^{-6}$ mol g^{-1}.

The absence of the ν(=C–H) band of *cis*-2-butene in spectrum h in Fig. 6 is conclusive evidence for the occurrence of the following addition reaction in the adsorbed state as well as in the gas phase.



(R) . (4)

The observation of the esr spectrum of a nitroxide as shown in Fig. 8 is further support of this reaction. On introducing *cis*-2-butene onto a surface which has a rather large amount of adsorbed nitrogen dioxide, the esr intensity of the organic nitroxide shown in Fig. 8 grows, while that of the NO_2 decreases, suggesting the formation of a species like $R_2\dot{N}O$ from R, a precursor of this nitroxide radical, shown in reaction equation (4). The ir absorption spectrum i may be identified with this radical species. It is thus concluded that the reaction expressed by the rate equation (3) occurs by the same radical mechanism as that proposed for the gas phase reaction, where the addition of NO_2 to the olefin is the rate-determining step (*5*).

For the unsteady reaction of high rate, expressed by kinetic equation (2), the same reaction path is essentially applicable as discussed above. The activation energy determined for k_{in} was 5.5 kcal mol^{-1}. This is considered to agree fairly well with 4 kcal mol^{-1}, the energy barrier for rotation about the central C–C bond of the intermediate, R (*26*). Therefore, the rotation step is considered to be the rate-controlling process of the unsteady reaction. If the double bond of *cis*-2-butene is already loosened prior to the addition of NO_2, the activation energy of the reaction (4) must be decreased, and therefore it is possible for the rotation step to govern the overall reaction rate. This supposition is supported by the following observations. On the surface with only the nitrite type of adsorbed NO_2, the adsorbed *cis*-2-butene gives the olefinic C–H stretching band with a 6 cm^{-1} red shift, as observed in ir spectrum g in Fig. 6. This indicates that the double bond of the butene is loosened by its interaction with an electronically deficient site on the surface. Such sites are probably the acid sites. The presence of π-complexed butene on acid sites of the porous Vycor glass has been suggested (*27*). Considering the fact that dbm isomerization occurs even though it is poisoned by less than $\{NO_2\} = 20 \times 10^{-6}$ mol g^{-1} of adsorbed nitrogen dioxide, and that the esr of NO_2 radical measured at room temperature suggests its interaction with hydroxyl groups on the glass, it is probable that the butene molecules interacting with the acid sites react with the NO_2 molecules interacting with these sites. Provided that the sites are easily saturated by butene adsorption, it can be explained that the reaction is zero order in the pressure of *cis*-2-butene. The contribution of the nitrite species to the reaction is not clear at present, but the adsorbed butene may also interact with it.

The esr spectrum identified with the nitroxide radical, is difficult to observe when the value of $\{NO_2\}$ is small. However, the rate of accumulation of the nitroxide radical, which is estimated from the rate of the increase in the intensity of esr absorption, strongly depends on $\{NO_2\}$ when this is rather large. Therefore, it is suspected that the nitroxide radicals or their polymers block the acid sites, causing the reduction of the reaction rate in the earlier stage, if $\{NO_2\}$ has a large value.

Infrared observations suggest that most adsorbed nitrogen dioxide contains some type of N_2O_4. If the equilibrium expressed by Eq. (1) is established between the surface concentrations of the species, NO_2 and N_2O_4, the following relation may hold.

$$[NO_2] = (K_s[N_2O_4])^{\frac{1}{2}} \simeq (K_s\{NO_2\}/2)^{\frac{1}{2}},$$

where K_s the equilibrium constant of Eq. (1) on the surface. Thus a rate of isomerization with the rate-controlling step of Eq. (4) is also consistent with a dependence on the square root of $\{NO_2\}$. However, in this study, such an equilibrium cannot be established, because the thorough evacuation of gaseous nitrogen dioxide was accomplished, as described in the Procedure section. The esr observation assures that the amount of NO_2 radical is proportional to $\{NO_2\}$.

Since the dimensions of the catalyst are fairly large and its pore radius is on the other hand small (20 Å), the effectiveness factor for the kinetic data should be accounted for by the theory for reactions having Langmuir–Hinshelwood or general order kinetics (*29*, *30*). The Thiele moduli estimated for the reaction in the later stage were at most 0.03. Provided the rates in the earlier stages are a hundred times as high as those in the later stage, the moduli are not more than 0.3, corresponding to the effectiveness factor of unity (*29*).

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