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The *cis-trans* Isomerization of 2-Butenes Photosensitized by Adsorbed Acetone

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The anomalous acceleration of the rate of the *cis-trans* isomerization of 2-butenes is observed in the photosensitization of acetone adsorbed on porous Vycor glass. The anomaly is explained by means of a chain mechanism which is compatible with the triplet-triplet energy transfer mechanism. The chain carrier may be radicals formed by the dissociation of the lowest triplet acetone, resulting from the less efficient quenching of the triplet acetone by butenes at lower butene pressures. The preferential quenching of the acetone by the *cis* isomer to by the *trans* isomer of 2-butenes suggests that the geometrical factor plays a significant role in the reaction in the adsorption phase.

It was shown in a previous report[1] that the photosensitized isomerization of 2-butenes by ketones adsorbed on porous Vycor glass proceeds by means of the mechanism of the triplet-triplet energy transfer from ketones to 2-butenes. At a low pressure of 2-butenes, anomalously high rates of isomerization have been observed when acetone is used as a sensitizer. This anomaly cannot be explained in terms of the reaction scheme proposed previously.[1] We intend to report here the details of the isomerization of 2-butenes photosensitized by the adsorbed acetone on the porous Vycor glass and to suggest a mechanism for interpreting the anomaly mentioned above.

Experimental

The properties and the pretreatment of the porous Vycor glass, and the apparatus and the method used in the photosensitized isomerization, were identical with those described in the previous report.[1] The light from a Toshiba H-400-P medium-pressure mercury lamp was filtered by passing it through 1-cm path of water and a Toshiba UV-29 glass filter (transparent >270 nm), so that the adsorbed acetone was excited to its lowest singlet state. The adsorption of acetone and the sensitized reaction were carried out at room temperature. The amount of acetone remaining in the gas phase was negligibly small during the course of the reaction.

The *cis*-2-butene was a high-purity product of the Phillips Petroleum Co. The *trans*-2-butene and 1-butene were purchased from Takachiho Kagaku Kogyo Co. The butenes were further purified by trap-to-trap distillation in a high-vacuum apparatus. A spectro-pure-grade acetone obtained from Wako Pure Chemical Industries, Ltd., was purified in a similar manner. The nitric oxide was an extra-pure-grade product of the Takachiho Kagaku Kogyo Co. and was used without further purification.

Results and Discussion

The illumination of the porous Vycor glass plate on which acetone has been preadsorbed induces the *cis-trans* isomerization of 2-butenes without any double-bond migration reaction. Using 100% of *cis*-2-butene as the starting material, the initial rates of *trans*-2-butene formation, $R^0_{c\text{-}t}$, were obtained at the various amounts of the adsorbed acetone. Figure 1 shows the relation between $R^0_{c\text{-}t}$ and I, the relative light intensities absorbed by acetone at different coverages ($\theta = 0.13 \sim 0.49$). The proportionality between them guarantees that the *cis-trans* isomerization will be sensitized by adsorbed acetone.

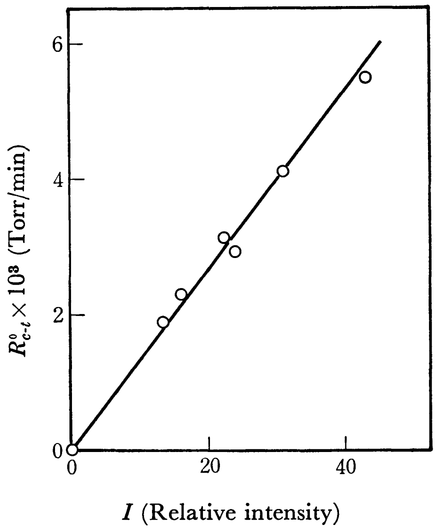

Fig. 1. The relation between $R^0_{c\text{-}t}$ and I.
The initial pressure of *cis*-2-butene, $P^0_{c\text{-}B}$ is 120 Torr.

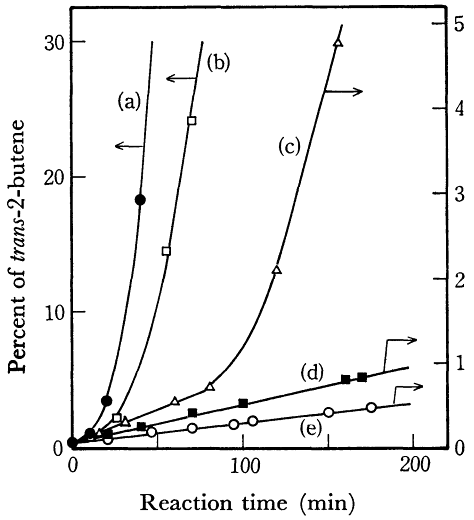

Fig. 2. The time-courses of the photosensitized isomerization at various $P^0_{c\text{-}B}$.
The coverage of the adsorbed acetone, θ_A, is 0.24.
(a); 14 Torr, (b); 18 Torr, (c); 41 Torr, (d); 80 Torr, (e); 125 Torr.

The time-course of the formation of *trans*-2-butene at different initial pressures of *cis*-2-butene are indicated in Fig. 2. At high pressures, *trans*-2-butene is formed at a constant rate, while at pressures less than ~40 Torr the rate of the *trans* isomer formation is accelerated. Although the scattering of the incident light by the porous adsorbent results in an inaccurate estimate of the absolute quantum yield, the roughly calculated values for the *trans*-2-butene formation after the acceleration, for instance, for the curves of (a) or (b) in Fig. 2, exceed 10 at a reaction time longer than 40 min. However, those for the data at high butene pressures never exceed unity.

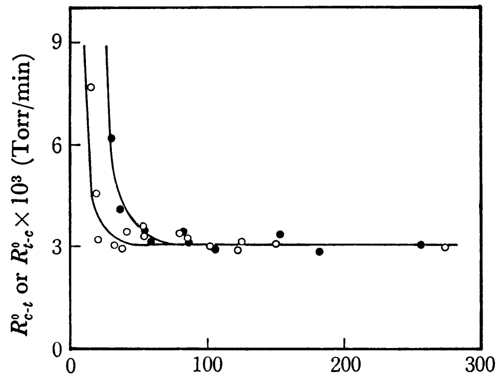

Fig. 3. The effect of butene pressure on the initial rate of the photoisomerization.
$\theta_A = 0.24$, —○—; $R^0_{c\text{-}t}$, —●—; $R^0_{t\text{-}c}$.

The pressure effect on $R^0_{c\text{-}t}$ and $R^0_{t\text{-}c}$, the initial rate of *cis*-2-butene formation from 100% *trans*-2-butene, is indicated in Fig. 3. The rates observed at low pressures show a very steep increase with a decrease in the pressure, and $R^0_{t\text{-}c}$ is always greater than $R^0_{c\text{-}t}$, while at high pressures of butenes neither rate depends on the pressure and both give the same value.

The most general mechanism for the photosensitized *cis-trans* isomerization by acetone on the solid surface is given by the following processes:[1]

$$^0\mathrm{A(a)} \xrightarrow{h\nu} {}^1\mathrm{A(a)} \longrightarrow {}^3\mathrm{A(a)} \tag{1}$$

$$^3\mathrm{A(a)} \longrightarrow {}^0\mathrm{A(a)}\ \ (+\text{heat or } h\nu) \tag{2}$$

$$^3\mathrm{A(a)} + {}^0\mathrm{A(a)} \longrightarrow 2\,{}^0\mathrm{A(a)} \tag{3}$$

$$^3\mathrm{A(a)} + t\text{-}{}^0\mathrm{B(a)} \longrightarrow {}^0\mathrm{A(a)} + {}^3\mathrm{B(a)} \tag{4}$$

$$^3\mathrm{A(a)} + c\text{-}{}^0\mathrm{B(a)} \longrightarrow {}^0\mathrm{A(a)} + {}^3\mathrm{B(a)} \tag{5}$$

$$^3\mathrm{B(a)} \longrightarrow \alpha\cdot t\text{-}{}^0\mathrm{B(a)} + (1-\alpha)\cdot c\text{-}{}^0\mathrm{B(a)} \tag{6}$$

where ^{0}A and ^{3}B represent the ground-state acetone and the triplet 2-butene respectively, when the other symbols have their usual meanings,[1] and where the suffix (a) indicates the adsorbed state of the individual species.

Steady-state approximations for ^{3}A(a) and ^{3}B(a) give the following equations:

$$R^0_{t\text{-}c} = (1-\alpha)I_0\phi_{\mathrm{isc}}k_4[t\text{-}{}^0\mathrm{B}]/(k_2+k_3[{}^0\mathrm{A}]+k_4[t\text{-}{}^0\mathrm{B}]) \tag{7}$$

$$R^0_{c\text{-}t} = \alpha I_0\phi_{\mathrm{isc}}k_5[c\text{-}{}^0\mathrm{B}]/(k_2+k_3[{}^0\mathrm{A}]+k_5[c\text{-}{}^0\mathrm{B}]) \tag{8}$$

Here, the quantum yield of ^{3}A(a) or ϕ_{isc} must be close to unity, as has been verified in the liquid phase.[2] The independence of both rates from the change in the butene pressure at $P^0_{t\text{-B}} > \sim 60$ Torr and $P^0_{c\text{-B}} > \sim 40$ Torr, as is shown in Fig. 3, may reasonably be ascribed to the triplet-energy transfer by means of Eq. (4) or (5) being faster than that by the deactivation (Eqs. (2) and (3)).[1] The proportionality between $R^0_{c\text{-}t}$ and I also suggests that Process (3) is slow compared to Process (5) or (4).

The rapid increase in the rates and the anomalously high quantum yield in the low-pressure range can not be explained only by Processes (1)~(6). The difference between the photostationary state ratio, $([t\text{-}{}^0\mathrm{B}]/[c\text{-}{}^0\mathrm{B}])_{\mathrm{pss}}$, at a high pressure of butene, 2.8~3.0, and that at a low pressure, 2.2~2.4, suggests that the dominant mechanisms for the two pressure ranges are different. The following mechanism conceivably predominates in the low-pressure range:

$$^3\mathrm{A(a)} \longrightarrow \mathrm{R\cdot(a)} \tag{9}$$

$$\mathrm{R\cdot(a)} + c\text{-}{}^0\mathrm{B(a)} \longrightarrow \mathrm{R\text{-}B\cdot(a)} \tag{10}$$

$$\mathrm{R\cdot(a)} + t\text{-}{}^0\mathrm{B(a)} \longrightarrow \mathrm{R\text{-}B\cdot(a)} \tag{11}$$

$$\mathrm{R\text{-}B\cdot(a)} \longrightarrow \mathrm{R\cdot(a)} + \beta\cdot t\text{-}{}^0\mathrm{B(a)} + (1-\beta)\cdot c\text{-}{}^0\mathrm{B(a)} \tag{12}$$

$$\mathrm{R\cdot(a)} + \mathrm{R\cdot(a)} \longrightarrow \mathrm{P(a)} \tag{13}$$

where R· is presumably the methyl or acetyl or a reactive product produced from these radicals; R–B·, a complex between 2-butene and R· in which the π-bond opening of butene may be established, and P, the termination product of R·. The *cis-trans* conversion occurs in Process (12), accompanying a regeneration of the chain carrier, R·. It is conceivable that, at low butene pressures, the formation of the chain carrier, R·, from the triplet acetone (Process (9)) becomes remarkable, since the efficiency of the triplet quenching by butenes (Process (4) or (5)) is low. The assumptions that the chain carrier, R·, and, accordingly, R–B·, accumulate with the time give an explanation for the accelerating rate and the high quantum yield mentioned above. The acceleration appears in the earlier stage of the reaction for lower pressures of butenes because of the fast accumulation of radicals. The abnormally high rates in the low-pressure range (Fig. 3) must be attributed to the difficulty of obtaining the initial rate, excluding the contribution of the chain mechanism, because of a rapid acceleration.

In the course of the reaction at the butene pressure of 86 Torr, the butene in the gas phase was condensed by means of a liquid-nitrogen trap at Point (A) in Fig. 4, followed by a sudden vaporization after 15 min at (B). The very rapid formation of *trans*-2-butene is seen in the first analysis of the butenes after Point (B). Then, the reaction proceeded steadily, with a velocity identical with that observed before the condensation. The rapid formation of *trans*-2-butene in Fig. 4 may also be caused by the accumulation of R· during the condensation of butene in the gas phase. The addition of 0.7 Torr of nitric oxide to 17.3 Torr of *cis*-2-butene prevented the acceleration of the rate, and the *trans*-2-butene production proceeded proportionally with the time under the low conversion, as had been seen at high pressures of butene.[3] This suggests that the R· must be captured by Process (14) resulting in no accumulation of the radicals:

$$\mathrm{R\cdot} + \mathrm{NO} \longrightarrow \mathrm{RNO} \longrightarrow \text{stabilized} \tag{14}$$

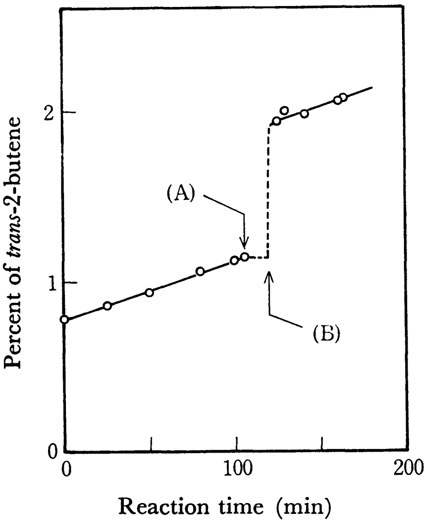

Fig. 4. The effect of condensation of butenes during the photoisomerization.
$P^0_{c\text{-}t}=86$ Torr, $\theta_A=0.24$
At point (A); condensation, (B); vaporization.

At pressures of butene higher than 60 Torr, the ratio of $R^0_{c\text{-}t}$ to $R^0_{t\text{-}c}$ is unity (Fig. 3). Then, the blanching ratio, α, is obtained as 0.5 from Eq. (15):

$$R^0_{c\text{-}t}/R^0_{t\text{-}c} = \alpha/(1-\alpha) = 1.0 \qquad (15)$$

k_5/k_4 was estimated to be 2.8~3.0 from Eq. (16):

$$([t\text{-}^0\mathrm{B}]/[c\text{-}^0\mathrm{B}])_{\mathrm{pss}} = (k_5/k_4)(\alpha/(1-\alpha)) = 2.8\sim3.0 \qquad (16)$$

In the liquid phase, the ratios of the quenching rate constant for the *cis* and *trans* isomers of 2-pentene sensitized by acetone were estimated to be 1.0 and 1.30 by Borkman and Kearns[2b)] and Saltiel *et al.*[5)] respectively. In contrast to these results, we have concluded that the preferential quenching by the *cis* isomer occurs in the adsorbed layer. This is consistent with the result that the contribution of the chain mechanism is remarkably more pronounced in $R^0_{t\text{-}c}$ than in $R^0_{c\text{-}t}$ under the same pressure (See the low-pressure range in Fig. 3). Although the features of the complex formation in the quenching of acetone by 2-butenes are not clear at present, the difference in the geometrical structures of 2-butene isomers may play an important role in establishing the ease of such complex formation so far as the reaction in the adsorbed layer is concerned.

References

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3) The appreciably lower rate than the constant value at high butene pressure was observed by addition of nitric oxide, since nitric oxide is an effective quencher for the triplet ketones.[4)]

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