BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (9), 2335—2336 (1974)

# The Photosensitized Isomerization of 2-Butenes by Sensitizers Adsorbed on Porous Vycor Glass

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(Received December 26, 1973)

**Synopsis.** The triplet-triplet energy transfer from ketones adsorbed on the Vycor glass to 2-butenes was rapid enough for us to neglect the transfer to the surface when the transfer is exothermic. Different photoisomerization mechanisms were suggested for different groups of sensitizers.

The photochemical behavior of electronically-excited molecules adsorbed on the solid surface is considerably different from that in the gas or solution phase.[1]

The photosensitized *cis-trans* isomerizations of olefins have been studied in detail in a homogeneous system; these studies have led to a considerable increase in our understanding of the triplet-triplet energy transfer mechanism.[2] However, the mechanism of the photoisomerization by the electronically-excited molecules adsorbed on the solid surface has not yet been well understood.

In this brief note, we intend to report on a study of the *cis-trans* photoisomerization of 2-butenes using various kinds of adsorbed molecules as sensitizers and to discuss the effect of the adsorption on the reaction.

## Experimental

*Adsorbent.* A porous Vycor glass plate ($30\times9\times1$ mm, Corning 7930, surface area of 144 $m^2/g$) used as an adsorbent is transparent in the ultraviolet region down to about 200 nm. Its transparency and large surface area are advantageous for the UV-spectra measurement of the adsorbed molecules and for the kinetic investigation of the sensitized isomerization. Prior to every run of the experiments, the glass was calcined with dried air in a reactor and degassed at 650 °C *in vacuo* for 2 hr.

*Materials.* The compounds used as sensitizers were extra pure reagents obtained from Tokyo Kasei Kogyo Co., Ltd., or Wako Pure Chemical Industries, Ltd. The sulfur dioxide was an anhydrous product of Matheson Chemical Co.

*Procedure.* The photoisomerization of 2-butenes was carried out using a closed gas-circulation apparatus capable of achieving a vacuum down to $10^{-6}$ Torr. Vycor glass plates on which sensitizers has been adsorbed with a coverage of 0.25 at most were irradiated by means of a Toshiba H-400-P medium-pressure mercury lamp. The light was filtered by passing it through a 1 cm path of water and one of the following glass filters: (1) Corning 7—54 (transparent 230—410 nm), (2) Toshiba UV-29 (transparent >270 nm), and (3) Toshiba UV-35 (transparent >320 nm). The choice of filter depends on the sensitizers used for exciting the molecules to their lowest singlet states. The adsorption of sensitizers and the photoisomerization of 2-butenes were carried out at room temperature.

## Results and Discussion

The Vycor glass plate degassed at temperatures lower than 600 °C catalyzed the thermal isomerization of butenes, while it became negligible at 650 °C.

Upon irradiation, the adsorbed acetone, methylethyl ketone, pyrazine, acetophenone, biacetyl, nitrobenzene, and sulfur dioxide sensitized the photoisomerization of 2-butenes without any double-bond migration. Without irradiation, the isomerization did not occur on the Vycor glass where one of those compounds has been adsorbed; this was checked before and after carrying out the photosensitized isomerization. The adsorbed benzene, toluene, naphthalene, phenol, aniline, and *p*-dichlorobenzene could catalyze the *cis-trans* isomerization as well as the double-bond migration appreciably. However, irradiation increased the rate of *cis-trans* isomerization only.[3]

The simplest general scheme for a sensitized *cis-trans* photoisomerization over the solid surface is given by Eqs. (1)—(7), by analogy with the homogeneous reaction,[4] where $^0S(a)$, $^1S(a)$, and $^3S(a)$ are the adsorbed

$$^0S(a) \xrightarrow{h\nu} {}^1S(a) \tag{1}$$

$$^1S(a) \longrightarrow {}^0S(a) \tag{2}$$

$$^1S(a) \longrightarrow {}^3S(a) \tag{3}$$

$$^3S(a) \xrightarrow{\text{surface}} {}^0S(a) \tag{4}$$

$$^3S(a) + t\text{-}^0B(a) \longrightarrow {}^0S(a) + X^*(a) \tag{5}$$

$$^3S(a) + c\text{-}^0B(a) \longrightarrow {}^0S(a) + X^*(a) \tag{6}$$

$$X^*(a) \longrightarrow \alpha\cdot t\text{-}^0B(a) + (1-\alpha)\cdot c\text{-}^0B(a) \tag{7}$$

sensitizers in the ground, lowest singlet, and lowest triplet states respectively, and where $c$-$^0B(a)$ and $t$-$^0B(a)$ are adsorbed *cis*- and *trans*-2-butene in the ground states respectively. $X^*(a)$ represents an unspecified common intermediate which produces *trans*-2-butene with a probability of $\alpha$.

Starting from 100% of *cis*-2-butene, the initial rate of *trans* isomer formation, $R_0$, can be written as follows;

$$R_0 = \alpha I_0\phi_{\text{isc}}\cdot[c\text{-}^0B]/(k_4/k_6+[c\text{-}^0B]) \tag{8}$$

where $I_0$ is the light intensity absorbed by a sensitizer on the Vycor glass, and where $\phi_{\text{isc}}$ is the quantum yield of intersystem crossing for the sensitizer. $I$, the relative light intensity absorbed by a sensitizer, was calculated by the combination of the UV-absorption spectra of the adsorbed sensitizer with the radiative intensity distribution of the arc and the transmission of the combined filters. The relative quantum yields of *cis* to *trans* isomerization ($R_0/I$) for the sensitizers obtained at an initial *cis*-2-butene pressure of 50 Torr are plotted against the lowest triplet energies ($E_T$) of the sensitizers in Fig. 1.[5]

The relative quantum yields for ketones and pyrazine[6] increased sharply at an $E_T$ value of about 77 kcal/mol, which is very close to that of 2-butenes.[11] This shows that the triplet-triplet energy-transfer mech-

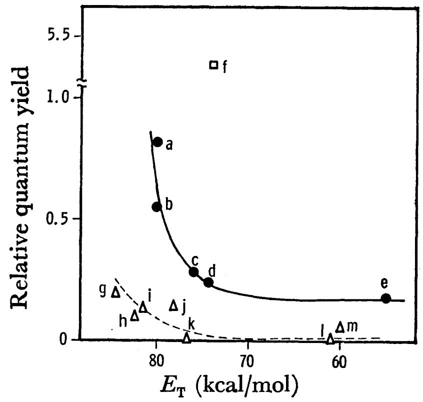

Fig. 1. The relative quantum yield as a function of the triplet energy of the sensitizers.
a, methyl-ethyl-ketone; b, acetone; c, pyrazine; d, acetophenone; e, biacetyl; f, sulfur dioxide; g, benzene; h, toluene; i, phenol; j, *p*-dichlorobenzene; k, aniline; l, naphthalene; m, nitrobenzene.

anism must be favored when the triplet state of a sensitizer has a higher energy than that of 2-butenes. In this case, X*(a) represents the adsorbed 2-butene in the triplet state.

It has been shown that the triplet-triplet energy transfer occurs upon every collision if the transfer is exothermic in the gas phase.[12)] This is valid also for stilbene and piperylene in the solution phase.[4)] On the solid surface, however, since adsorbed triplet molecules are always in contact with the surface, the energy dissipation to the surface, Eq. (4), may compete effectively with Eq. (5) or (6). To examine this, the pressure effect on the rates of photoisomerization was studied with acetone as a sensitizer. The relation between the initial rates of *trans*-2-butene formation and the pressures of *cis*-2-butene is shown in Fig. 2. The rates do not depend on the pressure. The coverage of adsorbed 2-butenes was confirmed to be less than unity when the pressure was lower than about 300 Torr. These results show that Reaction (6) is fast enough for us to neglect the (4) process in this case.

The fairly high isomerization yield for biacetyl, even though its triplet energy is as low as 54.9 kcal/mol,[13)] implies that a different intermediate is produced. Presumably, the Schenck mechanism[14)] predominates in this case.

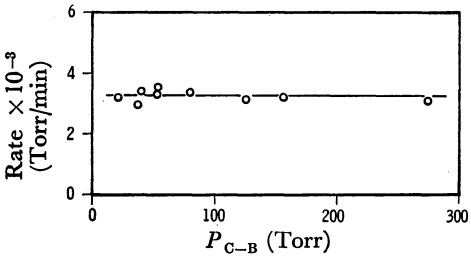

Fig. 2. The effect of pressure of *cis*-2-butene on the rate of photoisomerization.

Naphthalene, benzene, and its derivatives showed low quantum yields compared to those of ketones, as may be seen in Fig. 1. The correlation between the quantum yield and $E_T$ is not so clear as that found for ketones. If the energy transfer from the excited singlet state to the surface occurs rapidly, the low isomerization yield may be attributed to the inefficient triplet formation of sensitizers.[15)] On the other hand, if this process is not competitive with the intersystem crossing, it is conceivable that the low isomerization yield may be caused by a relatively faster triplet energy transfer to the surface than to 2-butenes.

The isomerization yield for sulfur dioxide was extremely high compared to those of the other compounds examined. A rough estimation of the absolute quantum yield gave about 5 for this compound. This high quantum yield suggests that the reaction proceeds *via* a chain mechanism.

Additional study is still needed before the role of adsorption can be clarified definitively for the above sensitized photoisomerization. However, we would like to stress that the mechanisms on the surface are quite different among the groups of sensitizers.

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2) For a review see N. J. Turro, "Molecular Photochemistry," Benjamin, New York, (1967), p. 178.

3) Irradiation with the light of wavelength about 250 nm to the bare surface caused the isomerization to some extent, and its rate was proportional to the intensity of incident light. In the cases of benzene, toluene, phenol, and *p*-dichlorobenzene as sensitizers, the light of this wavelength region was included. However, more than 90% of incident light was absorbed by the sensitizers, and the contribution from the bare surface to the total reaction can be neglected.

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5) The contributions of thermal isomerization in the cases of naphthalene, benzene, and its derivatives were subtracted from the total reaction rates.

6) $\phi_{\text{isc}}$ for these compounds can be taken as unity. This is valid for acetone,[7)] acetophenone,[8)] biacetyl,[9)] and pyrazine[10)] in the liquid phase.

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