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Isomerization of *cis*-2-Butene Caused by Electronically-excited Sulfur Dioxide ($^3B_1$) Adsorbed on Porous Vycor Glass

Kiyoshi OTSUKA, Masaki FUKAYA, and Akira MORIKAWA

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

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The *cis-trans* isomerization of *cis*-2-butene caused by electronically-excited sulfur dioxide has been studied at the gas-solid interface of porous Vycor glass. All of the quantum yields for the isomerization obtained gave values larger than $\approx$30. Infrared studies show that the product on the glass is the polysulfone formed through the copolymerization of sulfur dioxide and *cis*-2-butene. These results and the kinetic data for the isomerization can be explained satisfactorily by the proposed mechanism in which the isomerization occurs through the addition and elimination of 2-butene molecules at the terminal of the polysulfone formed on the glass; the copolymerization is initiated by an electronically-excited SO_2 ($^3B_1$) state.

The photochemistry of sulfur dioxide is of special interest to the scientist who is concerned with the rates and mechanisms for the removal of sulfur dioxide in sunlight-irradiated atmospheres. There is substantial evidence that the harmful effect of sulfur dioxide on health is enhanced when there are significant levels of suspended particulates in polluted atmospheres.[1] This leads to a consideration of the effect of suspended particulates on photochemical reactions involving sulfur dioxide, through excitation due to the absorption of sunlight in the first allowed absorption band ($SO_2(^1B_1) \leftarrow SO_2(\tilde{X}, {}^1A_1)$), which extends from 340 to 240 nm.

The chemical reactions between photochemically-excited sulfur dioxide and olefin hydrocarbons have been studied by a number of investigators.[2—9] All these studies, however, have been limited to homogeneous systems of gas or liquid phase, and there appear to be no published studies on these reactions at the gas-solid interface.

Recently, Otsuka *et al.* have reported that sulfur dioxide adsorbed on porous Vycor glass catalyzes the geometrical isomerization of 2-butenes.[10] The rate of this reaction is enhanced to a great extent by ultraviolet irradiation. Hence, in this report, the isomerization of *cis*-2-butene induced by electronically-excited sulfur dioxide over porous Vycor glass is described in detail. This system can be regarded as a very basic model of the system which involves the atmospheric reaction of sulfur dioxide with olefins over solid particulates in sunlight-irradiated atmospheres. Porous Vycor glass was chosen as the solid adsorbent because of its large surface area and high transparency to ultraviolet radiation down to wavelengths of about 210 nm, which is advantageous for ultraviolet spectral measurements of the adsorbed molecules and for a kinetic investigation of the photo-excited adsorbed molecules'

Experimental

The porous Vycor glass (Corning No. 7930, $30 \times 8 \times 1$ mm plate, surface area $= 149$ m^2/g), sulfur dioxide, *cis*-2-butene and apparatus used were described previously.[10]

Procedure. Before each run, the porous Vycor glass (0.50 g) placed in the reactor was calcined at 600 °C in dried oxygen and then degassed for 2 h in a vacuum down to about 8×10^{-5} Torr at the same temperature. Following the introduction of sulfur dioxide into the reactor, which was maintained at a given temperature, the reaction was initiated by irradiating the glass immediately after introducing the *cis*-2-butene and circulating the sulfur dioxide-*cis*-2-butene gas mixture through the reactor. A small amount of the reacting gases was periodically collected for analysis by gas chromatography, and the amount of *trans*-2-butene produced was determined. The ultraviolet light generated by a Toshiba H-400-P medium-pressure mercury lamp was filtered upon passage through 1 cm of water, a Corning 7-54 glass filter and either a Toshiba UV-29 (transparent to 270—410 nm) or a UV-31 (290—410 nm) glass filter. The temperature of the reactor was controlled to within ±0.2 °C using the air or water bath shown in Fig. 1.

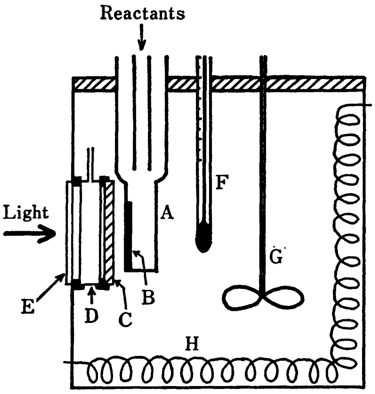

Fig. 1. Schematic diagram of the reaction system. A: Reaction vessel, B: porous Vycor glass, C: glass filters, D: water filter, E: quartz window, F: thermometer, G: stirrer, and H: electric heater.

Estimation of Absorbed Light Intensities and Quantum Yields. The emission intensity distribution of the mercury lamp (from Toshiba Technical Data No. 21-HM-11) and the transmission of the combined filters provided the energy distribution of the incident light, $I_0(\lambda)$. The relative light intensity absorbed by the sulfur dioxide adsorbed on the glass, I_r, was calculated using the equation,

$$I_r = \int_0^\infty I_0(\lambda)\left\{1-\frac{T(\lambda)}{100}\right\}\left\{\frac{D_{SO_2}(\lambda)}{D_{SO_2}(\lambda)+D_G(\lambda)}\right\}d(\lambda),$$

where $D_{SO_2}(\lambda)$ and $D_G(\lambda)$ are the optical densities of the adsorbed sulfur dioxide and of the porous glass, at wavelength λ, respectively,[11] and $T(\lambda)$ is the transmittance of the glass-sulfur dioxide system.

A quantitative determination of the incident light intensity at the cell face was made employing potassium ferrioxalate actinometry, and the absolute light intensity absorbed by sulfur dioxide, I_a, was calculated using the equation,

$$I_a = I_i I_r \Big/ \int_0^\infty I_0(\lambda)\mathrm{d}(\lambda),$$

where I_i is the incident light intensity at the cell face. The absolute quantum yield of the isomerization of *cis*-2-butene is given by $R_{c\to t}/I_a$, where $R_{c\to t}$ is the rate of geometrical isomerization.

Results

The cis-trans *Isomerization of* cis-*2-Butene.* The light of wavelength longer than 270 nm applied in this study induces no reaction of *cis*-2-butene in the absence of sulfur dioxide. If sulfur dioxide is present on the porous Vycor glass, selective *cis-trans* isomerization occurs thermally.[10] The initial rate of this thermal isomerization, $R^T_{c\to t}$, or the rate of *trans*-2-butene formation, is plotted against the amount of adsorbed sulfur dioxide, V_{SO_2}, in Fig. 2, where the experiments were carried out at 25 °C at an initial pressure of *cis*-2-butene of 150 Torr.

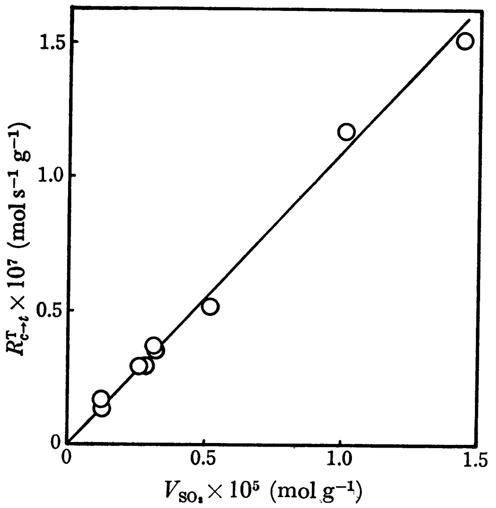

Fig. 2. Plot of the rate of thermal isomerization, $R^T_{c\to t}$, *vs.* the amount of sulfur dioxide adsorbed, V_{SO_2}, at $P_{cis\text{-but}}=105$ Torr; the reactions were carried out at 25 °C.

Ultraviolet irradiation of the glass, onto which sulfur dioxide had been adsorbed, markedly accelerated the rate of isomerization. The rate of photo-induced isomerization, $R^P_{c\to t}$, calculated from the difference between the rate measured under irradiation and $R^T_{c\to t}$, was obtained for various *cis*-2-butene pressures and amounts of adsorbed sulfur dioxide. Figure 3 shows the plot of $R^P_{c\to t}$ as a function of the *cis*-2-butene pressure. $R^P_{c\to t}$ does not depend on the pressure for pressures higher than 100 Torr. The effect of V_{SO_2} on $R^P_{c\to t}$ is indicated in Fig. 4. It has been confirmed in advance that the sulfur dioxide preadsorbed on the glass does not desorb after the addition of *cis*-2-butene for the experimental conditions under which the data in Figs. 3 and 4 were obtained.

The relative quantum yields of isomerization for the data in Fig. 4 are plotted against the amount of adsorbed sulfur dioxide in Fig. 5. It can be seen that the quantum yield decreases with the amount of sulfur dioxide adsorbed. The estimated absolute quantum yield, $R^P_{c\to t}/I_a$, for the lowest value in Fig. 5 is about 30. This high quantum yield suggests that the reaction proceeds *via* a chain process.

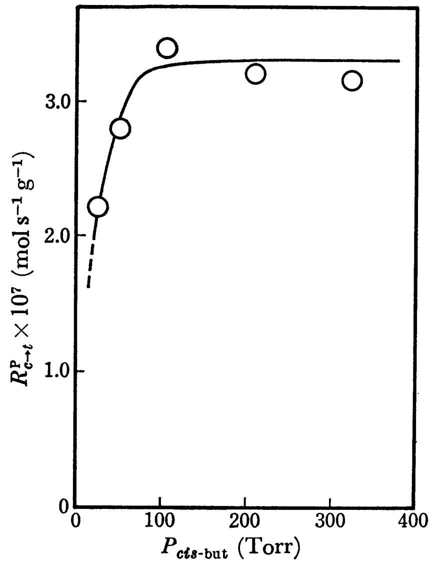

Fig. 3. Plot of the rate of photo-induced isomerization, $R^P_{c\to t}$, *vs.* the pressure of *cis*-2-butene, $P_{cis\text{-but}}$. The filters were Corning 7-54 and UV-31 filters. The amount of sulfur dioxide adsorbed is 2.5×10^{-6} mol/g; the reactions were carried out at 25 °C.

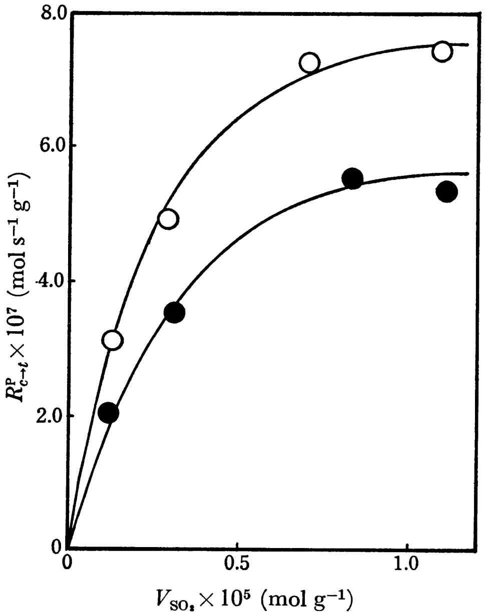

Fig. 4. Plot of $R^P_{c\to t}$ *vs.* V_{SO_2}, at $P_{cis\text{-but}}=105$ Torr and at 25 °C. Filters: (○); Corning 7-54 and UV-29, and (●); Corning 7-54 and UV-31.

The addition of a small amount of nitric oxide (0.77×10^{-5} mol) to a system of sulfur dioxide (0.55×10^{-5} mol) and *cis*-2-butene (1.44×10^{-3} mol) completely poisons the photo-induced isomerization, suggesting that the reaction intermediate is a radical.

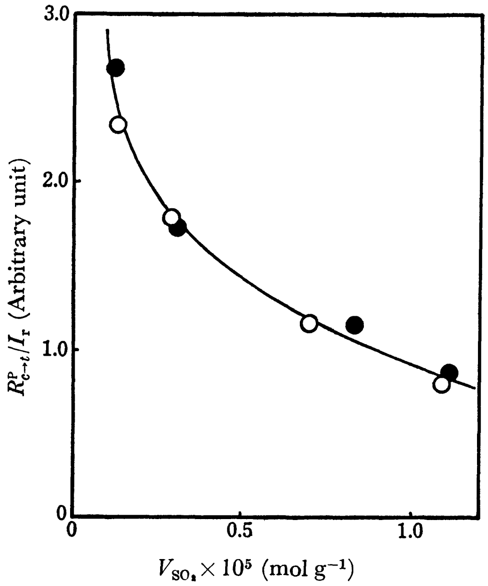

Fig. 5. Plot of the relative quantum yield of the photo-induced isomerization, $R^P_{c\to t}/I_r$, as a function of the amount of adsorbed sulfur dioxide. Filters: (○); Corning 7-54 and UV-29, and (●); Corning 7-54 and UV-31.

The Copolymerization of Sulfur Dioxide with cis-*2-Butene.* All the experiments described in this section were carried out with a sulfur-dioxide concentration (2.1×10^{-3} mol) compared to that applied in the preceding section ($<1.3\times 10^{-5}$ mol).

After a photo-induced geometrical isomerization for 150 min at 0 °C, the product on the glass was extracted with dioxane. The solution was dropped onto a KBr film and the dioxane solvent was evaporated. After several repetitions of this procedure, the infrared spectrum of the film was recorded (Fig. 6). This spectrum exhibits the two characteristic absorption bands of the polysulfone from *cis*-2-butene, one at 1300 cm^{-1} and the other at 1105—1140 cm^{-1} due to the symmetrical and asymmetrical stretching vibrations of the sulfone group, respectively.[12)]

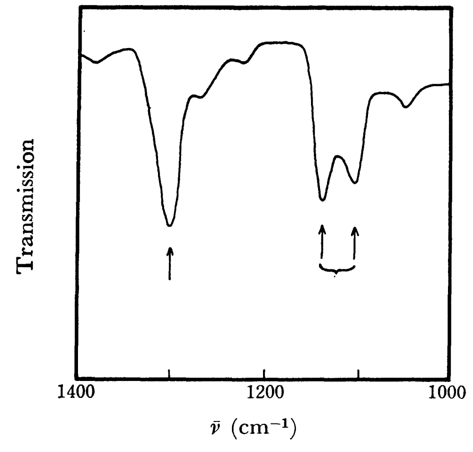

Fig. 6. Infrared spectrum of the polysulfone formed on the glass from *cis*-2-butene and sulfur dioxide under irradiation. The reaction was carried out at 0 °C under initial pressures of *cis*-2-butene and sulfur dioxide of 105 Torr (2.10×10^{-3} mol).

During the progress of the isomerization, the pressure decrease due to the reaction of SO_2 with *cis*-2-butene on the glass was followed by reading a glass Bourdon gauge at different temperatures. After the initial rapid adsorption, no reactants were consummed in the gas phase when the temperature was higher than ≈40 °C. However, a considerable consumption of gas was observed at low temperatures (<20 °C). Without irradiation, no gas consumption was detected after the initial adsorption for all temperatures in the range from 0 to 60 °C. The average rate of gas consumption under irradiation for times of 10—30 min, $\Delta V_g/\Delta t$, and the rate of photo-induced isomerization are plotted as a function of temperature in Fig. 7. The rate of isomerization has a maximum value at just the temperature for which the consumption of reactants becomes negligible (≈30 °C). It was shown that at a low sulfur-dioxide concentration (0.15×10^{-5} mol) the rate of isomerization decreases monotonically with a rise in temperature from 0 to 70 °C.

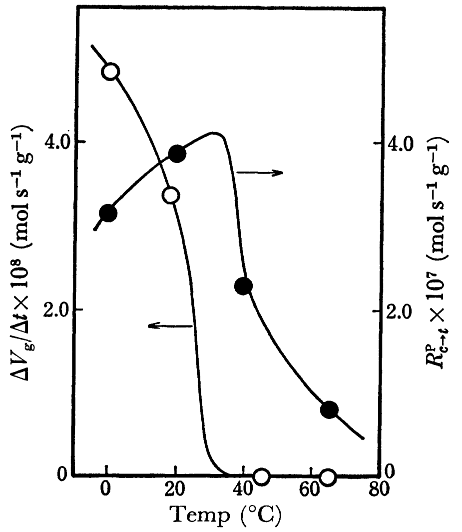

Fig. 7. Temperature effects on the rate of gas consumption, $\Delta V_g/\Delta t$, and on that of photo-induced isomerization, $R^P_{c\to t}$, (○); $\Delta V_g/\Delta t$ and (●); $R^P_{c\to t}$. The initial pressures of *cis*-2-butene and sulfur dioxide were 105 Torr.

Discussion

Many studies of the gas-phase photolysis of sulfur dioxide-olefin hydrocarbon mixtures have suggested that electronically-excited sulfur dioxide sensitizes the geometrical isomerization of the olefins.[4,6–9,13–17)] Furthermore, it has been observed that the $^3B_1$ state of sulfur dioxide is the only excited electronic state of sulfur dioxide participating in the geometrical isomerization of 2-butenes,[6,8,9)] 1,2-dichloroethylenes,[13)] 1,2-difluoroethylenes,[14,15)] and 2-pentenes.[16,17)] In these gas-phase studies, however, the absolute quantum yield for isomerization never exceeds unity. The high quantum yields (>30) obtained in the present work cannot be explained by means of the mechanism proposed for the photosensitized isomerization in the gas phase.

Bristow and Dainton first observed that irradiated mixtures of *cis*- or *trans*-2-butene in liquid sulfur dioxide result in a fast *cis-trans* isomerization, in addition to the polysulfone formation *via* the copolymerization of SO_2 and 2-butene.[3] The formation of polysulfone over glass confirmed in the present work (Fig. 6) suggests that the isomerization at the gas-solid interface occurs *via* a mechanism similar to that proposed for the reaction in the liquid phase.[3]

Assuming $^3B_1$ is the only electronically-excited state of SO_2 initiating the copolymerization, the following mechanism is proposed:[3,10]

$$SO_2 + h\nu \xrightarrow{I_a} {}^1SO_2({}^1B_1),$$

$${}^1SO_2({}^1B_1) + cis\text{-2-butene}$$

$$\longrightarrow {}^3SO_2({}^3B_1) + cis\text{-2-butene}, \tag{1}$$

$$\longrightarrow SO_2 + cis\text{-2-butene}, \tag{2}$$

$${}^3SO_2({}^3B_1) + cis\text{-2-butene} \longrightarrow P_s + P_b, \tag{3}$$

$$\longrightarrow SO_2 + trans\text{- or } cis\text{-2-butene}, \tag{4}$$

$$P_s + cis\text{-2-butene} \longrightarrow P_b, \tag{5}$$

$$P_b + SO_2 \longrightarrow P_s, \tag{6}$$

$$P_b \longrightarrow P_s + trans\text{-2-butene}, \tag{7}$$

$$\longrightarrow P_s + cis\text{-2-butene}, \tag{8}$$

$$P_s \longrightarrow P_b + SO_2, \tag{9}$$

$$P_b \longrightarrow \text{stabilized}. \tag{10}$$

$$P_s \longrightarrow \text{stabilized}, \tag{11}$$

where the mechanism is considered for a low isomerization conversion rate and a low sulfur-dioxide concentration compared to those for *cis*-2-butene. All species appearing in the above reactions are in the adsorbed layer. For low sulfur-dioxide concentrations the unimolecular decay of the $^1B_1$ and $^3B_1$ states of sulfur dioxide and the quenching of these states by ground-state sulfur dioxide molecules are unimportant[18,19] and have not been included in the above process. P_s and P_b represent the terminal group of active polysulfone ($P_s \rightarrow \dot{S}O_2CH(CH_3)CH(CH_3)\cdots\cdots\cdots SO_2CH(CH_3)\dot{C}H(CH_3) \leftarrow P_b$). The strong poisoning effect of nitric oxide must be due to the quenching of these terminal groups through a reaction with nitric oxide. The selective *cis-trans* isomerization occurs mainly through depropagation Steps 7 or 8 of the copolymerization since the contribution from Reaction 4 can be neglected because of the low quantum yield (<1.0).[8,9,15–17]

If the consumption of reactants during the isomerization is due to polysulfone formation, the results shown in Fig. 7 (open circles) indicate that the copolymerization of sulfur dioxide and *cis*-2-butene on the glass has a ceiling temperature around 30 °C. Above the ceiling temperature, the rates of the depropagation steps exceed those of the propagation steps and, thus, polymerization can no longer occur. The decrease in the rate of isomerization above the ceiling temperature (Fig. 7 closed circles) can reasonably be explained as a consequence of the decrease in the number of long-chain polysulfone sites necessary for the isomerization.

Dainton and Ivin have shown that the ceiling temperature for the polysulfone formation decreases with decreasing concentrations of comonomers.[22] The fact that, at low sulfur-dioxide concentrations, no maximum of the isomerization rate has been observed within the temperature range down to 0 °C, may be due to a shift of the ceiling temperature to a lower value below 0 °C.

According to the Reactions 1—11 indicated above, the rate of photo-induced isomerization can be described by Eq. i:

$$R^{\mathrm{P}}_{c\to t} = I_a k_7 \left(\frac{k_1}{k_1+k_2}\right)\left(\frac{k_3}{k_3+k_4}\right) \times \left\{\frac{2(k_5[cis\text{-2-but}]+k_9)+k_{11}}{k_{10}(k_5[cis\text{-2-but}]+k_9+k_{11})+k_{11}(k_6[SO_2]+k_7+k_8)}\right\}, \tag{i}$$

where the concentrations for *cis*-2-butene and sulfur dioxide are those on the surface, and I_a is the light intensity absorbed by sulfur dioxide on the glass; we have neglected the contribution of photo-sensitized isomerization (Reaction 4). At high *cis*-2-butene pressures ($>$100 Torr), it has been shown that the rate of isomerization is independent of the pressure (Fig. 3). This must be attributed to saturation of the active site on the glass by the chemically-adsorbed *cis*-2-butene which is involved in propagation Step 5.[23]

We can rearrange Eq. i to Eq. ii in order to observe the effect of the adsorbed sulfur-dioxide concentration, thus,

$$I_a/R^{\mathrm{P}}_{c\to t} = A + B[SO_2], \tag{ii}$$

where

$$A = \frac{(k_1+k_2)(k_3+k_4)}{k_1k_3k_7} \times \left\{\frac{k_{10}(k_5[cis\text{-2-but}]+k_9+k_{11})+k_{11}(k_7+k_8)}{2(k_5[cis\text{-2-but}]+k_9)+k_{11}}\right\}$$

and

$$B = \frac{(k_1+k_2)(k_3+k_4)}{k_1k_3k_7}\left\{\frac{k_6k_{11}}{2(k_5[cis\text{-2-but}]+k_9)+k_{11}}\right\}.$$

At high *cis*-2-butene pressures ($>$100 Torr), A and B can be regarded as constant (Fig. 3). Using the data in

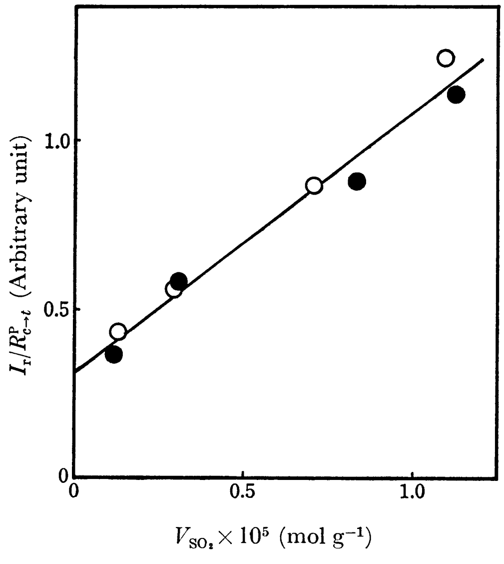

Fig. 8. Plot of $I_r/R^{\mathrm{P}}_{c\to t}$ *vs.* V_{SO_2}. Filters: (○); Corning 7-54 and UV-29, (●); Corning 7-54 and UV-31.

Fig. 4, which were obtained in experiments carried out at a constant *cis*-2-butene pressure of 105 Torr, $I_r/R^p_{c\to t}$ is plotted against the amount of adsorbed sulfur dioxide in Fig. 8. A reasonably good linear relation between these variables supports the proposed process.

As described above, all the results and the kinetic data obtained in this work can be explained satisfactorily by the reaction mechanism in which the geometrical isomerization of *cis*-2-butene accompanies the copolymerization of sulfur dioxide with *cis*-2-butene, which is initiated by the electronically-excited $^3B_1$ state of sulfur dioxide.

References

1) U. S. Dept. of Health, Education, and Welfare, "Air Quality Criteria for Sulfur Oxides," Public Health Service, Consumer Protection and Environmental Health Service, National Air Protection Control Administration, Washington, D. C. (1969); NAPCA publication No. AP-50.

2) F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, **46**, 374, 382 (1950).

3) G. M. Bristow and F. S. Dainton, *Proc. R. Soc. London, Ser. A*, **229**, 525 (1955).

4) R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **56**, 1211 (1960).

5) E. Cehelnik, C. W. Spicer, and J. Heicklen, *J. Am. Chem. Soc.*, **93**, 5371 (1971).

6) R. D. Penzhorn and H. Güsten, *Z. Naturforsh.*, **27a**, 1401 (1972).

7) R. A. Cox, *J. Photochem.*, **2**, 1 (1973—1974).

8) K. L. Demerjian, J. G. Calvert, and D. L. Thorsell, *Int. J. Chem. Kinet.*, **6**, 829 (1974).

9) K. L. Demerjian and J. G. Calvert, *Int. J. Chem. Kinet.*, **7**, 45 (1975).

10) K. Otsuka, K. Eshima, and A. Morikawa, *Bull. Chem. Soc. Jpn.*, **50**, 631 (1977).

11) The ultraviolet spectra of the sulfur dioxide-*cis*-2-butene system adsorbed on porous Vycor glass has been studied in detail in a preceding paper.[10] When sulfur dioxide coadsorbs with *cis*-2-butene, the absorbance for the first allowed transition, $SO_2(^1B_1)\leftarrow SO_2(\tilde{X}, {}^1A_1)$, is enhanced in the long wavelength region by the proximity of the π-donating *cis*-2-butene molecules. As a consequence of this, the threshold of the absorption band shifts to a longer wavelength of about 420 nm.

12) R. E. Cook, F. S. Dainton, and K. J. Ivin, *J. Poly. Sci.*, **26**, 351 (1957).

13) F. B. Wampler and J. W. Bonttenheim, *Int. J. Chem. Kinet.*, **8**, 585 (1976).

14) F. B. Wampler, *Int. J. Chem. Kinet.*, **8**, 511 (1976).

15) F. B. Wampler, *Int. J. Chem. Kinet.*, **8**, 519 (1976).

16) F. B. Wampler, *Int. J. Chem. Kinet.*, **8**, 935 (1976).

17) F. B. Wampler, *Int. J. Chem. Kinet.*, **8**, 945 (1976).

18) H. W. Sidebottom, C. C. Badcock, J. G. Calvert, G. W. Reinhardt, B. R. Rabe, and E. K. Damon, *J. Am. Chem. Soc.*, **93**, 2587 (1971).

19) T. N. Rao, S. S. Collier, and J. G. Calvert, *J. Am. Chem. Soc.*, **91**, 1609 (1969).

20) R. D. Snow and F. E. Frey, *J. Am. Chem. Soc.*, **65**, 2417 (1943).

21) F. S. Dainton and G. M. Bristow, *Nature*, **172**, 804 (1953).

22) F. S. Dainton and K. J. Ivin, *Proc. R. Soc. London, Ser. A*, **212**, 207 (1952).

23) Adsorption experiments for *cis*-2-butene on porous Vycor glass have shown that a considerable increase in the amount of adsorption with increasing pressure, even in the range between 100 and 200 Torr. This is natural since most of the *cis*-2-butene on the glass may be physically adsorbed. The chemisorption of *cis*-2-butene occurs presumably at the Al^{3+} site, which is an impurity in the glass.[10]