The Sulfur Dioxide Photosensitized cis-trans Isomerization of Butene-2 The Quenching Effect of Oxygen and Nitric Oxide

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Rate constants were determined for the quenching reaction of excited triplet sulfur dioxide ($^3SO_2$) with the typical triplet quenchers oxygen and nitric oxide, employing the sulfur dioxide photosensitized cis-trans isomerization of butene-2. While the rate constant for $^3SO_2$ quenching by nitric oxide ($k=7.8 \pm 1.9 \times 10^{10}$ liters/mole sec) is near the collision number, the rate constant for quenching by oxygen ($k=2.4 \pm 0.5 \times 10^8$ liters/mole sec) is surprisingly low. The possible significance of these quenching processes on aerosol formation in photochemical smog is discussed.

Introduction

The role of sulfur dioxide (SO_2) as a primary light absorber in air pollution has been of increasing interest in recent years [1]. Upon absorption of sunlight, reactive electronically excited states of SO_2 may be produced which can participate in the photochemical reactions of polluted air. The reactions of electronically excited SO_2 with saturated and olefinic hydrocarbons are particularly important because of their possible relevance for the formation of atmospheric aerosols as well as their contribution in the homogeneous removal of SO_2 from polluted atmospheres. The primary photophysical processes of the SO_2 molecule that occur in the wave length region between 2400 and 4000 Å have been studied extensively by several authors [2]. CALVERT et al. [2f, 3, 4] provided substantial evidence that the reactive species is almost exclusively triplet excited SO_2 which they produced either by direct absorption in the forbidden 3400 – 4000 Å band transition or by collisionally induced intersystem crossing from the singlet excited SO_2 obtained by absorption in the 2400 – 3400 Å band. Recently, some rate constants were published [5] for the quenching of excited SO_2 with atmospheric gases and air pollutants such as saturated and olefinic hydrocarbons. This publication prompts us to publish our data on the quenching reaction of excited SO_2 with oxygen and nitric oxide. Both gases — oxygen as an atmospheric component and nitric oxide as a primary air pollutant from combustion processes — are known as notorious triplet quenchers in photochemistry. We have measured the quenching rate of $^3SO_2$ with O_2 and NO by means of the SO_2 photosensitized cis-trans isomerization of butene-2, a method introduced by CUNDALL and PALMER [6].

Experimental

Apparatus

A conventional all glass gas phase photochemistry apparatus was employed in this investigation. To avoid mercury in the reaction system an oil diffusion pump was used. Greaseless O-ring stopcocks were used throughout the reaction as well as the handling sections. Pressures were measured with a glass Bourdon gauge as well as with a Barocel Electronic Manometer. An air cooled HBO 200 W (Osram) high pressure mercury arc lamp was used as a light source. To avoid UV radiation not present in the troposphere, the light of wave length below 3000 Å was eliminated with a 2 mm thick cutt off filter (Type WG 5, Schott & Gen.). The cylindrical quartz reaction cell (5 cm ⌀ × 15 cm) was connected with an all glass gas circulating pump [7] for the proper mixing of gases and to achieve a better sampling for the gas chromatographic analyses.

Compounds

Anhydrous sulfur dioxide, trans-2-butene, nitric oxide and oxygen (all Baker C. P. grade) as well as cis-2-butene (Matheson Co.), were all thoroughly degassed by bulb to bulb distillation and then used without further purification. Their purities were found to be better than 99% by G l c and mass spectrometric analysis.

Analysis

Through an O-ring stopcock the reaction cell was connected directly to a F-7 Gas Chromatograph (Perkin-Elmer) provided with a flame ionization detector. Direct sampling was possible with a sampling valve (sample valve loop 0.1 ml). Most of the analysis were carried out at room temperature on a 6 foot long steel column filled with 30% diethylene glycol + $AgNO_3$ on chromosorb R (60 – 80 mesh). In experiments in which 1-butene was measured, the separation of this compound from cis-2-butene was accomplished at room temperature with a tetraisobutylene on chromosorb R (60 – 80 mesh) column, and a column containing a

30% dimethyl formamide on sterchamol at 0 °C. Comparable results were obtained with the various columns.

Appropriate experiments were carried out to show that no significant isomerization occurred under our experimental conditions when any mixture of the various gases employed in this work was irradiated in the absence of SO_2. At no time were the various reaction mixtures condensed, since it was observed that, at least at high pressures, solid polymers appeared. No oil droplet formation was observed during a photolytical run; only a slight solid deposit appeared after an extended period of irradiation, which showed a peak absorption at 2400 Å as measured with a Cary 15 Spectrophotometer. Substitution of a cell by a clean one increased the isomerization rate but did not alter the overall results. In the quenching experiments conversions were usually kept well below 10%.

Spectroscopy

The triplet energies of cis- and trans-butene were determined by the oxygen perturbation method[8]. The $S_0 - T$ absorption of a saturated chloroform solution of cis- and trans-butene under 180 atm of oxygen pressure was measured with a Cary 15.

Results

The effect of irradiation time on the SO_2 photosensitized isomerization of cis- and trans-2-butene is shown in Figure 1. Various mixtures of SO_2 at 165 Torr with cis-2-butene at 11,2 Torr as well as a mixture of SO_2 at 165 Torr with trans-2-butene at 11.2 Torr were irradiated over extended periods of time. The initial trans → cis isomerization is about half that of the cis → trans rate. From both independent experiments a photostationary state with a trans/cis ratio of 3.0 ± 0.2 was reached. This value is at variance with that of 1.27 obtained by CUNDALL and PALMER[6], possibly due to the shorter wave length of light used in their investigation *.

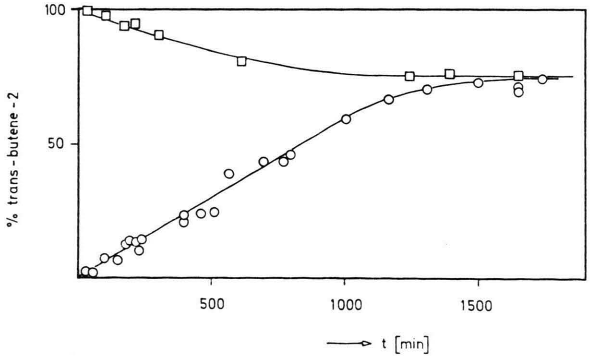

Fig. 1. Photochemical cis-trans isomerization of butene-2 at room temperature. cis- and trans-butene-2 at 11.2 Torr, SO_2 at 165 Torr, □ trans → cis, ○ cis → trans.

The occurrence of the slower trans → cis isomerization of butene-2 can be explained on the basis of the triplet energies of the involved species. With the oxygen perturbation method[8] we obtained from the $S_0 - T$ absorption for the triplet energy of trans-butene-2 > 76 kcal/mole and for cis-butene-2 70 ± 2 kcal/mole. The great error in these values arises from the fact that the precise determination of the $0 - 0$ absorption band is difficult to assign due to a lack of sufficient structure in the curves. A similar observation was made by MULLIKEN and ITOH[10]. Nevertheless, it can be concluded from our data and those of Mulliken that the triplet energy of trans-butene-2 is a few kcal/mole higher than that of SO_2 which is 73.4 kcal/mole[11].

Table 1 shows some experiments at constant SO_2 pressure and varying pressures of cis-butene-2.

Table 1. Photolysis of SO_2-cis-butene-2 mixtures at room temperature.

cC_4 * (Torr)	SO_2 (Torr)	cC_4/SO_2	R_t^0 (%) **
12.1	18.2	0.67	2.31
16.5	18.6	0.89	2.44
23.0	18.5	1.24	2.36
32.9	18.2	1.81	2.78
37.1	18.6	2.00	2.48
94.3	18.1	5.22	2.28

* cC_4 = cis-butene-2,
** R_t^0 is expressed as $[(tC_4/(tC_4+cC_4))] \cdot 100$, where tC_4 = trans-butene-2.

It is apparent that, within the cC_4/SO_2 ratios of $0.67 - 5.22$, the rate of trans-butene-2 formation is independent of the cis-butene-2 partial pressure. Only at very high conversions an additional gas chromatographic peak appeared (max 2%) which was identified as butene-1 from its retention time.

If inert quenchers, such as O_2 and NO, are added to constant SO_2 and butene-2 mixtures at various pressures, the $^3SO_2$ quenching efficiency of these gases can be measured. In independent experiments various mixtures of a) SO_2 ($7.6 - 28.5$ Torr) with cis-butene-2 ($5.8 - 11.7$ Torr) and NO ($5.9 - 140.3$ Torr); b) SO_2 (15 Torr) with cis-butene-2 (7 Torr)

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* A photostationary cis-/trans ratio of $1.2 - 3.0$ was recently found in the photosensitized cis-trans isomerization of cis-butene-2 by various photosensitizers in cyclohexane solution[9].

and O_2 (12.3 – 67.7 Torr) and c) SO_2 (295 Torr) with cis-butene-2 (6.7 Torr) and O_2 (80 – 150 Torr) were irradiated and the rate of isomerization was measured. The results of these quenching experiments can be seen plotted in Figure 2.

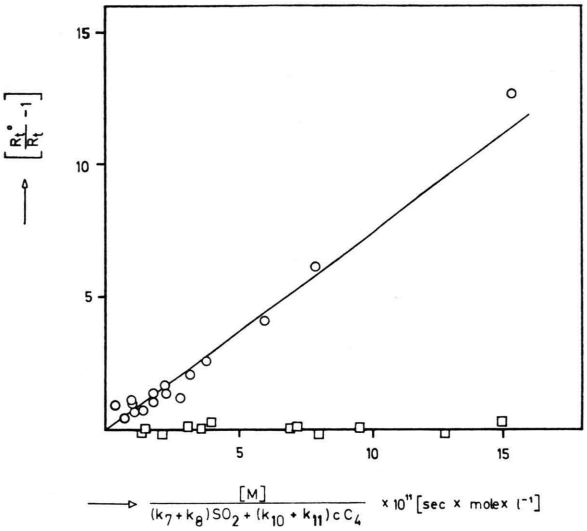

Fig. 2. ○ = NO; □ = O_2.
The quenching of $^3SO_2$ by NO and O_2 at room temperature.
Plot of $(R_t^0/R_t - 1)$ vs. $\dfrac{[M]}{(k_7+k_8)\,SO_2+(k_{10}+k_{11})\,cC_4}$.

From the slope of the straight lines, which are also predicted by the steady state approximation of the proposed reaction scheme (see discussion), the following rate constants were obtained for the quenching of $^3SO_2$ with NO and O_2:

$$k(\mathrm{NO}) = 7.8 \pm 1.9 \cdot 10^{10}\ \mathrm{l \cdot mole^{-1}\ sec^{-1}},$$
$$k(\mathrm{O_2}) = 2.4 \pm 0.5 \cdot 10^{8}\ \mathrm{l \cdot mole^{-1}\ sec^{-1}}.$$

Discussion

The currently accepted mechanism that describes the processes occurring in the excitation of SO_2 within the 2400 – 3400 Å band in the presence of other molecules is that proposed by CALVERT et al.[3, 4]. In the light of this mechanism, the following equations are appropriate to describe the photochemistry of SO_2-olefine mixtures **:

$$SO_2 + h\nu\ (>3000\ \text{Å}) \rightarrow {}^1SO_2 \qquad \text{(I)}$$
$$^1SO_2 + SO_2 \rightarrow {}^3SO_2 + SO_2 \qquad (1)$$
$$^1SO_2 + SO_2 \rightarrow 2\ SO_2 \qquad (2)$$
$$^1SO_2 + cC_4 \rightarrow {}^3SO_2 + cC_4 \qquad (5)$$
$$^1SO_2 + cC_4 \rightarrow SO_2 + cC_4 \qquad (6)$$
$$^1SO_2 \rightarrow SO_2 + h\nu_f \qquad (a)$$
$$\rightarrow SO_2 \qquad (b)$$
$$\rightarrow {}^3SO_2 \qquad (c)$$
$$^3SO_2 \rightarrow SO_2 + h\nu_p \qquad (d)$$
$$\rightarrow SO_2 \qquad (e)$$
$$^3SO_2 + SO_2 \rightarrow SO_3 + SO \qquad (7)$$
$$^3SO_2 + SO_2 \rightarrow 2\ SO_2 \qquad (8)$$
$$^3SO_2 + cC_4 \rightarrow SO_2 \cdot C_4\ (\text{or } SO_2 + {}^3C_4) \qquad (10)$$
$$^3SO_2 + cC_4 \rightarrow \text{products} \qquad (11)$$
$$SO_2 \cdot C_4 \rightarrow SO_2 + cC_4 \qquad (12)$$
$$\rightarrow SO_2 + tC_4 \qquad (13)$$
$$\rightarrow SO_2 + 1 - C_4 \qquad (14)$$

where $^1SO_2$ and $^3SO_2$ correspond to the singlet and triplet excited SO_2, respectively, cC_4 or tC_4 stands for cis- or trans-butene-2, 1-C_4 corresponds to butene-1, and $^3C_4$ is a tripet excited butene-2. In this mechanism it was assumed that only $^3SO_2$ can induce cis-trans isomerization or the formation of other products like for instance sulfinic acids[13]. Strong evidence supporting the validity of this assumption was presented by OKUDA et al.[2f]. Our data on the triplet energies of cis- and trans-butene-2 provide a further argument in support of the theory that $^3SO_2$ is the main reactive species. Since the triplet energy of trans-butene-2 lies above and the triplet energy of cis-butene-2 lies about 4 kcal/mole below that of $^3SO_2$, it seems reasonable ***, on the basis of a triplet energy transfer model, that the rate of trans → cis is slower than the rate of the cis → trans isomerization (see Figure 1).

** A somewhat different mechanism involving two reactive singlet and two reactive triplet states of SO_2 was proposed by HEICKLEN et al.[12].

*** Our determination of the triplet energies of trans- and cis-butene-2 is not in line with the recent data of ALFIMOV et al.[14]. According to their data obtained with the method of phosphorescence "bracketing", the triplet energies of both isomers should differ from each other by no more than 1.7 kcal/mole. This is in contrast with our $S_0 - T$ absorption spectra for both isomers and the distinctly different initial rates in SO_2 photosensitized cis → trans and trans → cis isomerizaton of butene-2.

Application of steady state considerations to the proposed reaction scheme leads to the relation

$$\frac{R_t^0}{I_{\mathrm{abs}}} = \left(\frac{k_{13}}{k_{12}+k_{13}}\right)\left(\frac{k_{10}\,\mathrm{cC_4}}{(k_7+k_8)\,\mathrm{SO_2}+(k_{10}+k_{11})\,\mathrm{cC_4}}\right) \cdot \left(\frac{k_1\,\mathrm{SO_2}+k_5\,\mathrm{cC_4}}{(k_1+k_2)\,\mathrm{SO_2}+(k_5+k_6)\,\mathrm{cC_4}}\right) \qquad \mathrm{(I)}$$

in which R_t^0 is the rate of formation of trans-butene-2 and I_{abs} the absorbed light. In the derivation of Eq. (I) the unimolecular singlet and triplet internal conversions, phosphorescence, fluorescence and non collision induced intersystem crossing were neglected. These processes are too slow to compete with the bimolecular reactions at the pressures employed in our study. Since butene-1 did not amount to more than 2%, even at the highest conversions, reaction (14) was also neglected.

The rate of trans-butene-2 formation is independent of the cis-butene-2 partial pressure (Table 1). This result is not unexpected in view of the values measured by CALVERT et al. [3, 4] for

$$(k_7+k_8) = 3.9\times10^8\ \mathrm{l\cdot mole^{-1}\cdot sec^{-1}}$$

and $$(k_{10}+k_{11}) = 1380\times10^8\ \mathrm{l\cdot mole^{-1}\cdot sec^{-1}}$$

and the assumption that the fraction of collisionally induced spin inversion with SO_2 is comparable to that with cis-butene-2.

With the addition of inert quenchers to the SO_2-butene-2 system the following additional equations are required:

$$^1\mathrm{SO_2} + \mathrm{M} \rightarrow {}^3\mathrm{SO_2} + \mathrm{M}\,, \qquad (3)$$

$$^1\mathrm{SO_2} + \mathrm{M} \rightarrow \mathrm{SO_2} + \mathrm{M}\,, \qquad (4)$$

$$^3\mathrm{SO_2} + \mathrm{M} \rightarrow \mathrm{SO_2} + \mathrm{M}\,. \qquad (9)$$

The mechanism then leads to the equation

$$\left(\frac{R_t^0}{R_t} - 1\right) = \frac{k_9\,M}{(k_7+k_8)\,\mathrm{SO_2}+(k_{10}+k_{11})\,\mathrm{cC_4}} \qquad \mathrm{(II)}$$

provided the SO_2 pressure is kept constant and the fraction of collisionally induced spin inversion of M is comparable to that of SO_2 and cis-butene-2. R_t in Eq. (II) corresponds to the rate of trans-butene-2 formation in the presence of a quencher M. As predicted by Eq. (II) a straight line with the slope k_9 is obtained from a plot of $(R_t^0/R_t - 1)$ versus $M/(k_7+k_8)\,SO_2 + (k_{10}+k_{11})\,cC_4$ (Figure 2).

The quenching constant $k_9(\mathrm{NO}) = 7.8 \pm 1.9 \times 10^{10}$ $\mathrm{l\cdot mole^{-1}\ sec^{-1}}$ obtained from Figure 2, employing CALVERTS et al. [5] rate constants in the denominator of Eq. (II), agrees well with that of $k_9(\mathrm{NO}) = 7.4 \pm 0.3 \times 10^{10}$ $\mathrm{l\cdot mole^{-1}\ sec^{-1}}$ obtained recently by CALTERT et al. [5] from the decay of $^3SO_2$ in the presence of NO. The quenching constant $k_9(O_2) = 2.4 \pm 0.5 \times 10^8\ \mathrm{l\cdot mole^{-1}\cdot sec^{-1}}$ derived from Fig. 2 is higher than that reported by CALVERT et al. [5] of $k_9(O_2) = 0.96 \pm 0.05 \times 10^8\ \mathrm{l\cdot mole^{-1}\cdot sec^{-1}}$, but clearly substantiates his observation that oxygen is a surprisingly inefficient $^3SO_2$ quencher. While the quenching constant for $^3SO_2$ by nitric oxide is near the collision number ($\sim 2\times10^{11}\ \mathrm{l\cdot mole^{-1}\ sec^{-1}}$) the quenching constant for $^3SO_2$ by O_2 is to our knowledge the lowest reported value for a triplet molecule quenching reaction by oxygen [15]. NO and O_2 are known as notorious triplet quenchers in photochemistry [15, 16]. According to the predictions of the quenching theory O_2 should even be a more powerful triplet quencher than NO [17].

The quenching rates of $\mathrm{Hg}(^3P_1)$ and $^3SO_2$ with NO, O_2 and N_2 are compared with each other in Table 2.

Table 2. Comparison of the quenching rates of $^3SO_2$ and $\mathrm{Hg}(^3P_1)$.

	NO	O_2	N_2
	$(\mathrm{l \times mole^{-1} \times sec^{-1}}) \times 10^{-10}$		
$^3SO_2$	7.8 [a]	0.024 [a]	0.0085 [b]
$\mathrm{Hg}(^3P_1)$	24.0 [c]	18 [c]	0.26 [c]

[a] This work, [b] Ref. [5], [c] Ref. [18].

As expected, NO and O_2 are much more efficient $\mathrm{Hg}(^3P_1)$ quenchers than N_2. The low quenching rate of $^3SO_2$ by O_2 may be explained by the electrophilic nature of both molecules. According to the quenching theory [15], a metastable collision complex between O_2 and the triplet state is a prerequisite for the quenching process. Furthermore, the efficiency of the complex formation and rapid quenching is controlled by the formation of charge-transfer states within the collision complex. Since NO has a higher electronic affinity than oxygen [19], i. e. is less electrophilic than O_2, the relative unimportance of the build-up of charge-transfer states in the $[^3SO_2 \cdot O_2]$ collision complex, due to the electrophilic nature of both molecules, may account for the ineffective quenching of $^3SO_2$ by O_2 and the comparatively effective quenching by NO.

SO_2 may disappear homogeneously from polluted atmospheres via $^3SO_2$ formed by direct absorption of sunlight or via the SO_3 produced during photooxydation. Both species can react with atmospheric components or pollutants and form stable products, such as sulfuric acid and possibly some sulfonic and sulfinic acids[20]. Renzetti and Doyle[21] observed that NO had a suppressing effect on aerosol formation. Since the reaction

$$SO_3 + NO \rightarrow SO_2 + NO_2$$

is endothermic, it might be speculated that a process like reaction (9) retards aerosol formation. Despite the fact that the $^3SO_2$ quenching rate with NO is 3.3×10^2 times larger than that with O_2 and that the quenching rate of NO is of the same order of magnitude than that of the olefines, reaction (9) can not effectively compete. Since the concentration of O_2 is at least by a factor 10^5 higher than that of NO in a polluted atmosphere, a competition will not be efficient. A conversion of NO to NO_2 seems to be a more likely prerequisite of aerosol build-up[22].

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