THE SULPHUR DIOXIDE PHOTOSENSITIZED *CIS–TRANS* ISOMERIZATION OF BUTENE-2

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SUMMARY

The photosensitized *cis–trans* isomerization of butene-2 in the presence of sulphur dioxide excited within its first allowed absorption band has been examined. Isomerization results primarily from the reaction of excited triplet SO_2 molecules ($^3SO_2$) with butene-2 although there is some evidence for a reaction of excited singlet SO_2 with *cis*-2-butene leading to isomerization. The quenching rate constants for $^3SO_2$ with *cis*-butene-2 and *trans*-butene-2 relative to SO_2 were determined from measurements of the quantum yields for photosensitized isomerization at high $[SO_2]/[\text{butene-2}]$ ratios. The rate constants for the reaction:

$$^3SO_2 + \text{butene-2} \, (\textit{cis or trans}) \rightarrow SO_2 + x \, \textit{trans}\text{-butene-2} + (1-x) \, \textit{cis}\text{-butene-2}$$
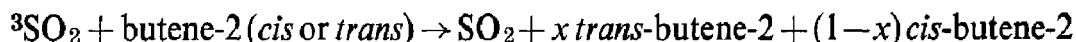
were $1.62 \pm 0.08 \times 10^{11}$ 1 mol^{-1} s^{-1} for the *cis* isomer and $1.42 \pm 0.09 \times 10^{11}$ 1 mol^{-1} s^{-1} for the *trans* isomer based on the literature value of 3.9×10^8 1 mol^{-1} s^{-1} for the absolute rate constant for the reaction of $^3SO_2$ with SO_2. The value of x, the fraction of *trans* isomer formed in the isomerization, was 0.587 ± 0.028.

The *cis–trans* isomerization of butene-2 provides a useful method for the determination of $^3SO_2$ yields in SO_2 photolysis in the first allowed absorption band. At the pressure and wavelength used in the present study, the quantum yield for the production of $^3SO_2$ molecules was 0.112 ± 0.006.

INTRODUCTION

In order to calculate the absolute amount of light absorbed by SO_2 in the cell a correction was made for reflective losses and also loss due to the non-parallel light beam. Considering the geometry of the system and using published data for reflective losses, the expected losses amounted to 30–40% of the transmitted light. Actinometric measurements of the transmitted light, I_t, and of the incident light, I_0 (with the reaction vessel removed and replaced by the actinometer cell) made at the end of the experimental work gave a loss factor of $I_0/I_t = 1.53$. The absorbed light intensity (in μEinsteins min^{-1}) was compared with the observed difference in photocell readings (mV) and a calibration factor of 1.36 μE min^{-1} mV^{-1} obtained. The absorbed light intensity (at 30 Torr SO_2) was 9.25×10^{16} photons min^{-1} and the estimated overall error in the quantum yields arising from the measurement of the light absorbed was $\pm$ 6%.

A Pye 'Series 104' gas chromatograph, equipped with a F.I.D. detector and a gas sampling valve, was used for gas chromatographic analysis of the butene-2 isomers. The *cis-* and *trans-*isomers were separated at room temperature on a 6 m column packed with dinonylphthalate on Celite. Calibration was carried out using samples of pure *cis-* and *trans-*butene-2 from the reaction cell using a standard sampling technique. The peak-area response was linear up to 15 Torr butene-2 in the reaction cell and the reproducibility for both calibration and reaction samples was better than $\pm$ 2% on successive samples. The calibration did not vary by more than 6% during the course of the experiments.

In a typical experiment the required gas mixture was made up in the previously evacuated cell and, after allowing to mix, a sample was withdrawn and analyzed to check the initial butene-2 composition. After irradiation, the cell contents were allowed to mix for 10–15 min and duplicate samples were analyzed. The amount of isomerization was determined from the increase in peak area of the *trans* (or the *cis*) isomer during the irradiation. In each case a correction was made for the sample removed from the reaction vessel. For the quantum yield determinations the extent of isomerization was kept as far as possible at less than 5%; when large conversions were obtained a small correction was made for the reverse reaction. The rate of isomerization was calculated in units of μmol min^{-1}.

In each experiment the light transmitted through the cell was measured with the photodiode. The difference in readings (mV) with and without the gas mixture present was converted to absorbed intensity (μEinsteins min^{-1}) using the calibration factor.
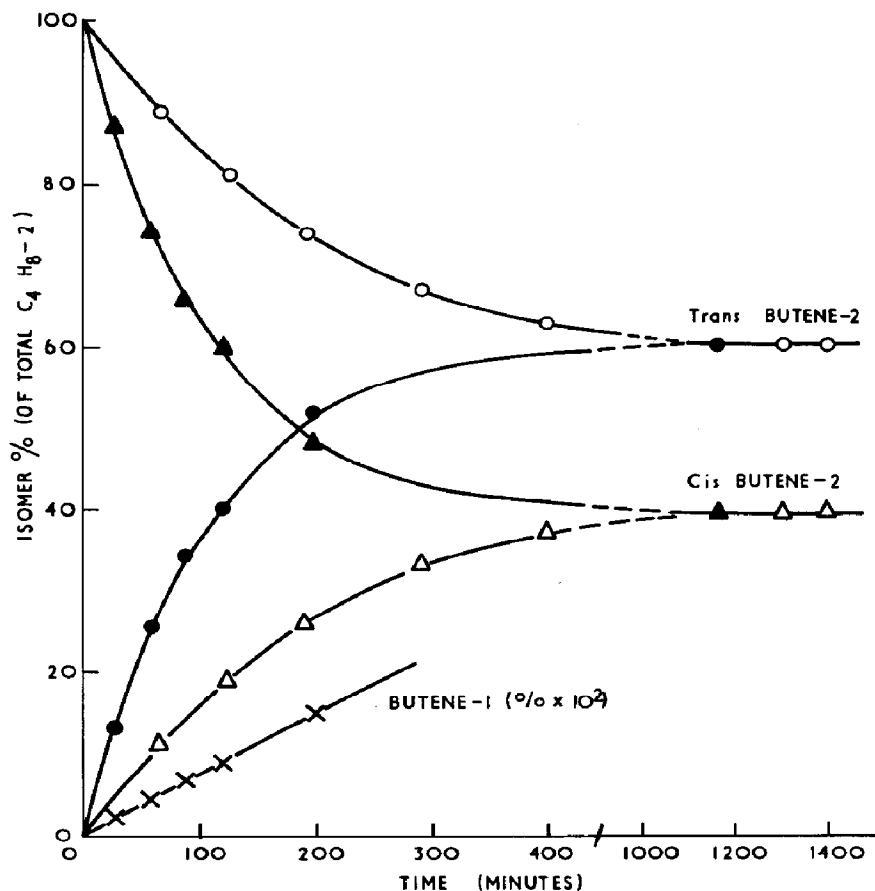
Fig. 1. The isomerization of butene-2 during the photolysis of SO_2–cis-butene-2 (filled points, $\lambda = 290$–330 nm) and SO_2–trans-butene-2 mixtures (open points, $\lambda = 311.5$ nm). Δ, cis-butene-2; O, trans-butene-2; X, butene-1 (measured in cis-butene-2–SO_2 photolysis only).

sorbed light intensity during the initial period was 0.71 μE/min. During the first 200 min samples were taken at regular intervals and duplicate samples were taken after overnight irradiation. A fast cis–trans isomerization reaction occurred with a much slower formation of butene-1. The isomerization reaction approached completion after 3 hours and, after overnight irradiation, a photostationary state was obtained with a final ratio of trans-butene-2/cis-butene-2 of 1.52. The same photostationary composition was obtained after prolonged irradiation of trans-butene-2 (0.32 Torr) with 32.5 Torr SO_2 using the 311.5 nm band.

In the experiment with cis-butene-2, the quantum yield for trans-butene-2 formation (Φ_T) in the initial stages was 0.103 and for butene-1 formation $\Phi(C_4H_8$–1$) = 1.4 \times 10^{-4}$. An estimate of the quantum yield for sulphinic acid formation was made from the decline in total butene concentration during the overnight irradiation. The value of Φ_{RSO_2H} was 7.0 $\times$ 10^{-3} which is lower than the value reported by Dainton and Ivin (33 $\times$ 10^{-3})[2].

A series of quantum yield determinations at 311.5 nm were made over a range of butene-2 pressures with an essentially constant SO_2 pressure of 31 ± 4 Torr*. Irradiation times were from 3 to 60 min depending on the amount of butene present. All experiments were conducted at 23 ± 2°C. Most of the determinations were made with *cis*-butene-2 present initially but a few measurements of the *trans* → *cis* isomerization were carried out. Table 1 shows the quantum yields for the various reaction conditions.
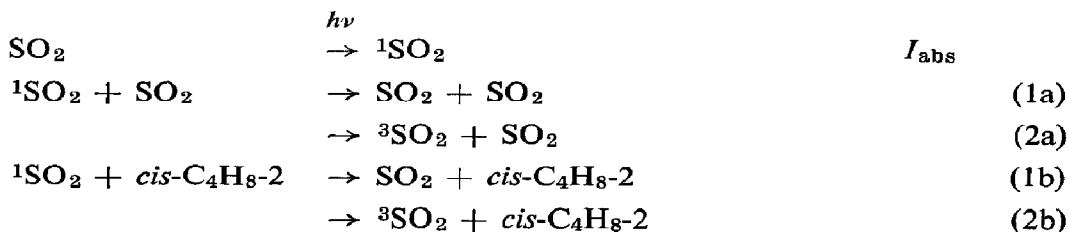
TABLE 1

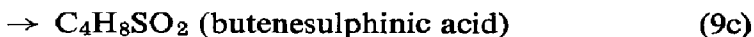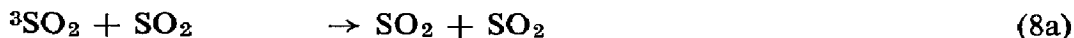QUANTUM YIELDS FOR THE SO_2 PHOTOSENSITIZED ISOMERIZATION OF *cis*-AND *trans*-BUTENE-2

Initial pressures (Torr)		Isomerization rate × 10^{-2} (μmol min^{-1})	I_{abs} (μEinstein min^{-1})	Quantum yield Φ_T (or Φ_C) × 10^{-2}
SO_2	Butene-2			
33.1	34.50 *(cis)*	3.16	0.159	19.90
32.4	15.60	2.40	0.162	14.80
28.4	13.03	2.41	0.152	15.80
31.8	7.70	2.31	0.172	13.40
28.2	4.37	1.53	0.144	10.64
34.4	2.38	1.72	0.172	10.00
29.4	1.05	1.23	0.156	7.84
29.9	0.495	0.920	0.159	5.78
30.3	0.300	0.822	0.161	5.12
30.2	0.215	0.775	0.161	4.83
30.7	0.108	0.648	0.163	3.97
30.5	0.086	0.575	0.163	3.52
29.8	0.065	0.486	0.153	3.18
30.6	0.039	0.366	0.163	2.24
31.1	0.340 *(trans)*	0.531	0.139	3.82
32.4	0.205 *(trans)*	0.433	0.139	3.11
32.5	0.078 *(trans)*	0.294	0.138	2.13
32.4	0.048 *(trans)*	0.242	0.149	1.62

DISCUSSION

Excitation of SO_2 in the first allowed absorption region leads to the formation of both excited singlet ($^1SO_2$) and triplet ($^3SO_2$) molecules. On the basis of previous work on SO_2 photochemistry, the following mechanism involving these states will be considered for discussion of the present results:

$$SO_2 \xrightarrow{h\nu} {}^1SO_2 \qquad\qquad\qquad\qquad I_{abs}$$

$$^1SO_2 + SO_2 \rightarrow SO_2 + SO_2 \qquad\qquad\qquad (1a)$$

$$\rightarrow {}^3SO_2 + SO_2 \qquad\qquad\qquad (2a)$$

$$^1SO_2 + cis\text{-}C_4H_8\text{-}2 \rightarrow SO_2 + cis\text{-}C_4H_8\text{-}2 \qquad (1b)$$

$$\rightarrow {}^3SO_2 + cis\text{-}C_4H_8\text{-}2 \qquad (2b)$$

* The SO_2 pressure was held constant to minimize uncertainties in the estimation of the absorbed light intensity.

$$^3SO_2 + SO_2 \qquad\qquad \rightarrow SO_2 + SO_2 \qquad\qquad\qquad\qquad\qquad (8a)$$

$$\rightarrow SO_3 + SO \qquad\qquad\qquad\qquad\qquad\qquad (8b)$$

$$^3SO_2 + cis\text{-}C_4H_8\text{-}2 \quad \rightarrow SO_2 + x\ trans\text{-}C_4H_8\text{-}2 + (1-x)\ cis\text{-}C_4H_8\text{-}2 \quad (9a)$$

$$\rightarrow SO_2 + C_4H_8\text{-}1 \qquad\qquad\qquad\qquad\qquad (9b)$$

$$\rightarrow C_4H_8SO_2 \text{ (butenesulphinic acid)} \qquad\qquad (9c)$$

$$^3SO_2 + trans\text{-}C_4H_8\text{-}2 \rightarrow SO_2 + x\ trans\text{-}C_4H_8\text{-}2 + (1-x)cis\text{-}C_4H_8\text{-}2 \quad (9')$$

Quenching of $^1SO_2$ by SO_2 and other gases occurs at a rate close to the collision frequency[6]. The fraction of collisions which result in $^3SO_2$ formation $[k_2/(k_1 + k_2)]$ depends on the nature of the collision partner[7] and, to a small extent on the excitation wavelength[8]. At 287.5 nm the fraction $k_2/(k_1 + k_2)$ is 0.095 ± 0.005, 0.073 ± 0.024 and 0.033 ± 0.008 for SO_2, cyclohexane and N_2 respectively[7]. No data are available for olefins. Quenching of $^3SO_2$ by SO_2 is a rather slow reaction[9] ($k_8 = k_{8a} + k_{8b} = 3.9 \pm 0.1 \times 10^8$ 1 mol^{-1} s^{-1}). Results from this laboratory[10] have indicated that only a small fraction ($\sim 4\%$) of the $^3SO_2$–SO_2 collisions result in chemical reaction to yield SO_3 i.e. $k_{8a} \cong 25\ k_{8b}$. Quenching of $^3SO_2$ by olefins, however, is very fast. Sidebottom et al.[4] obtained a value of $1.34 \pm 0.10 \times 10^{11}$ 1 mol^{-1} s^{-1} for the total quenching rate constant for cis-butene-2 ($k_{9a} + k_{9b} + k_{9c}$) which is close to the collision number.

From the present results it is clear that reactions (9b) and (9c) are only minor pathways compared to (9a). The rate of isomerization of cis-butene-2 at small conversions is therefore given by:

$$R_T = xk_9[^3SO_2]\ [cis\text{-}C_4H_8]$$

where $k_9 = k_{9a}$ and x is the fraction of the cis-butene-2 which is isomerized in reaction (9a). Application of steady state treatment for the concentrations of $^1SO_2$ and $^3SO_2$ yields the following expression:

$$R_T = xk_9[cis\text{-}C_4H_8] \Big\} \frac{(k_{2a}[SO_2] + k_{2b}[cis\text{-}C_4H_8])}{(k_8[SO_2] + k_9[cis\text{-}C_4H_8])} \times$$

$$\times \frac{I_{abs}}{(k_{1a} + k_{2a})[SO_2] + (k_{1b} + k_{2b})\ [cis\text{-}C_4H_8]} \Big\} \quad (i)$$

For high $[SO_2]/[cis\text{-}C_4H_8]$ ratios such that essentially all the $^1SO_2$ molecules are quenched by SO_2 the following expression may be derived for the quantum yield, Φ_T

$$\frac{1}{\Phi_T} = \frac{k_{1a} + k_{2a}}{xk_{2a}} \Big\{ \frac{k_8[SO_2]}{k_9[cis\text{-}C_4H_8]} + 1 \Big\} \quad (ii)$$

A similar expression can be derived for the quantum yield for *trans* → *cis* isomerization:

$$\frac{1}{\Phi_C} = \frac{k_{1a} + k_{2a}}{(1-x)k_{2a}} \left\{ \frac{k_8[SO_2]}{k_{9'}[trans\text{-}C_4H_8]} + 1 \right\}$$ (iii)

Figure 2 shows the quantum yield data plotted according to eqns. (ii) and (iii). A linear relationship was obtained for both the *cis* → *trans* and the *trans* → *cis* isomerization at $[SO_2]/[C_4H_8]$ ratios greater than 50. The rate constant ratios k_8/k_9 and $k_8/k_{9'}$ were determined from the slope/intercept ratios and the absolute values of k_9 and $k_{9'}$ were computed using the literature value[9] for k_8. Table 2 shows the quantities determined from Fig. 2, which confirm the very rapid quench-

TABLE 2

RATE CONSTANTS FOR $^3SO_2$ QUENCHING BY BUTENE-2 FROM FIG. 2

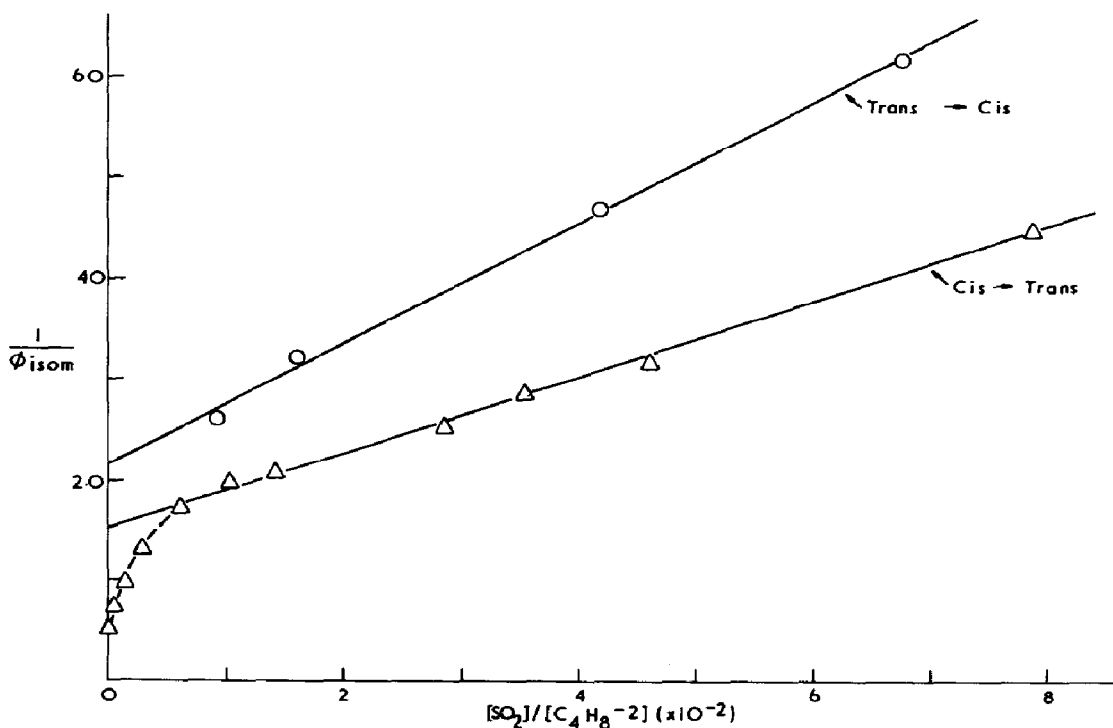| Olefin	Slope (S) × 10^{-2}	Intercept (I)	S/I × 10^{-3}	k_9 × 10^{11} (1 mol^{-1} s^{-1})
cis-C_4H_8	3.68 ± 0.10	15.3 ± 0.4	2.40 ± 0.09	1.62 ± 0.08
trans-C_4H_8	5.96 ± 0.22	21.7 ± 0.9	2.74 ± 0.15	1.42 ± 0.09

Fig. 2. Plot of the reciprocal of the quantum yield for photosensitized isomerization *vs.* the ratio of the initial pressures of SO_2 and butene-2 for the 311.5 nm photolysis of SO_2–butene-2 mixtures. (Initial pressure of SO_2 = 31 ± 3 Torr.)

ing of $^3SO_2$ by the butene-2 isomers*. The *cis* isomer appears to react slightly more rapidly than the *trans* isomer and the absolute value of k_9 is slightly higher than the value determined from phosphorescence quenching ($1.34 \pm 0.10 \times 10^{11}$ l mol^{-1} s^{-1})[4].

The intercepts of Fig. 2 may be used to determine x, the fraction of *trans*-2-butene formed in the quenching reaction (9), and the rate constant ratio $k_{2a}/(k_{1a} + k_{2a})$ *i.e.* the fraction of $^1SO_2$–SO_2 collisions which result in intersystem crossing.

The value obtained for x is 0.587 ± 0.028 indicating that formation of the *trans* isomer is favoured compared with the *cis* isomer. This result, combined with the slightly higher quenching rate constant for *cis*-C_4H_8-2, explains the observed *trans/cis* ratio in the equilibrium photostationary state after prolonged irradiation. At equilibrium:

$$(1-x)k_{9'} \, [trans\text{-}C_4H_8] = xk_9[cis\text{-}C_4H_8\text{-}2]$$

$$\frac{[trans]}{[cis]} = \frac{xk_9}{(1-x)k_{9'}} = 1.62 \pm 0.16$$

This compares well with the observed ratio of 1.52.

The rate constant ratio $k_{2a}/(k_{1a} + k_{2a})$ was 0.112 ± 0.006 which is slightly higher than previous estimates of this quantity at lower excitation wavelengths [7,8]. Previous studies have indicated that triplet sulphur dioxide production by reaction (2a) may depend on the excitation wavelength and, more recently, a dependence on total pressure has been found. The present value appears to be the first measurement at 311 nm and further work is required before the wavelength dependence of the $^3SO_2$ production rate can be ascertained.

It will be noted on Fig. 2 that the quantum yields at low $[SO_2]/[cis\text{-}C_4H_8]$ ratios ($\lesssim 30$) show a departure from eqn. (ii) in a sense that Φ_T increases rapidly as the $[SO_2]/[cis\text{-}C_4H_8]$ ratio decreases. For these conditions essentially all the $^3SO_2$ molecules are quenched by *cis*-C_4H_8-2 and eqn. (i) reduces to:

$$R_T = x \left\{ \frac{(k_{2a}[SO_2] + k_{2b}[cis\text{-}C_4H_8]) \, I_{abs}}{(k_{1a} + k_{2a}) \, [SO_2] + (k_{1b} + k_{2b}) \, [cis\text{-}C_4H_8]} \right\} \tag{iv}$$

which, by rearrangement gives:

$$\Phi_T \left\{ \frac{(k_{1a}+k_{2a})}{(k_{1b}+k_{2b})} \, \frac{[SO_2]}{[cis\text{-}C_4H_8]} + 1 \right\} = \frac{xk_{2a}}{k_{1b} + k_{2b}} \cdot \frac{[SO_2]}{[cis\text{-}C_4H_8]} + \frac{xk_{2b}}{k_{1b} + k_{2b}} \tag{v}$$

In order to test this relationship a knowledge of the relative total quenching rate constants for SO_2 and *cis*-C_4H_8 is required [*i.e.* the ratio $(k_{1a} + k_{2a})/(k_{1b} + k_{2b})$]. The fluorescence quenching measurements of Mettee[6a] showed that simple poly-

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* Error limits given refer to 95 % confidence limits from least squares analysis. The absolute error may be somewhat higher in view of the uncertainty associated with the light intensity measurement.

atomic gases quench $^1SO_2$ at closely similar rates. As a first approximation, therefore, the quantum yield data for $[SO_2]/[cis\text{-}C_4H_8] < 20$ were plotted according to eqn. (v) assuming $(k_{1a} + k_{2a})/(k_{1b} + k_{2b}) = 1$ (Fig. 3). Although there was some scatter in the data, an approximately linear relationship was obtained. The least squares regression line had a slope of 0.0856 ± 0.0036 and an intercept of 0.295 ± 0.024. Using $x = 0.587$ the value of the ratio $k_{2a}/(k_{1b} + k_{2b})$ [which on
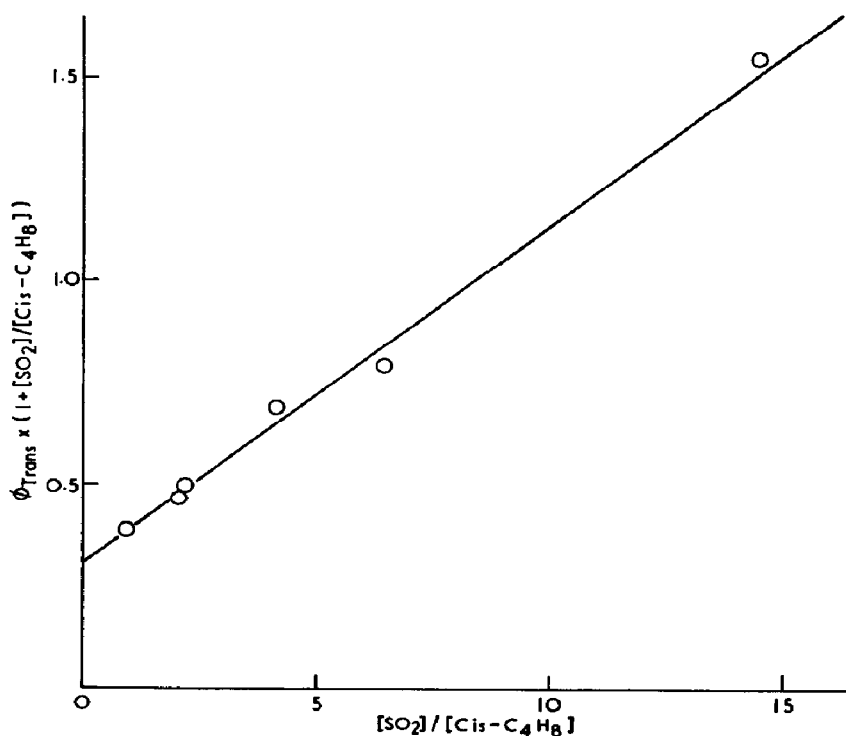

Fig. 3. Plot of the quantity $\Phi_{trans} \times \{ 1 + [SO_2]/[cis\text{-}C_4H_8]t$ vs. the ratio of the initial pressures of SO_2 and cis-2-butene for the 311.5 nm photolysis of SO_2–cis-butene-2 mixtures.

the above assumption is equal to $k_{2a}/(k_{1a} + k_{2a})$] derived from the slope is 0.146 ± 0.010 which is somewhat higher than the value derived from the data at high $[SO_2]/[cis\text{-}C_4H_8]$. The value of $k_{2a}/(k_{1a} + k_{2a})$ determined in this way is not very sensitive to the choice of the ratio $(k_{1a} + k_{2a})/(k_{1b} + k_{2b})$.

According to the mechanism chosen, the intercept on Fig. 3 gives a measure of the fraction of $^1SO_2$–cis-C_4H_8 collisions which result in intersystem crossing to $^3SO_2$. The value obtained for $k_{2b}/(k_{1b} + k_{2b})$ using $x = 0.587$ is 0.502 ± 0.048 which is unexpectedly high when compared to the value of 0.073 ± 0.024 found for cyclohexane, an organic molecule of similar molecular weight to cis-butene-2. However, it should be noted that this result depends on the chosen value of $(k_{1a} + k_{2a})/(k_{1b} + k_{2b})$.

The data for low $[SO_2]/[cis\text{-}C_4H_8]$ ratios could be equally represented by an equation analogous to eqn. (v) if, instead of reactions (1b) and (2b), a reaction between $^1SO_2$ and $cis\text{-}C_4H_8$ leading to isomerization is formulated:

$$^1SO_2 + cis\text{-}C_4H_8 \rightarrow SO_2 + x \; trans\text{-}C_4H_8 + (1-x)cis\text{-}C_4H_8 \qquad (2')$$
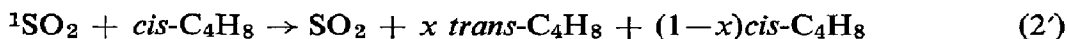
In this case the following expression is obtained:

$$\frac{\Phi_T}{x}\left\{\frac{k_{1a} + k_{2a}}{k_{2'}}\frac{[SO_2]}{[cis\text{-}C_4H_8]} + 1\right\} = \frac{k_{2a}}{k_{2'}}\frac{[SO_2]}{[cis\text{-}C_4H_8]} + 1 \qquad (vi)$$

Data plots of eqn. (vi) were made using several values of $(k_{1a} + k_{2a})/k_2$, in the range 0.5 to 4.0. The "best" fit of the data to eqn. (vi) (i.e. giving unit intercept) was obtained using $(k_{1a} + k_{2a})/k_{2'} = 2.7$. This is felt to be too high in view of the result of Sidebottom (unpublished measurements quoted in ref. 11) that the rate constant for $^1SO_2$ quenching by benzene is about twice that for SO₂. Using $(k_{1a} + k_{2a})/(k_{1b} + k_{2b}) = 0.5$ the values of $k_{2a}/(k_{1a} + k_{2a})$ and $k_{2b}/(k_{1b} + k_{2b})$ (on the basis of eqn. v) are 0.135 ± 0.012 and 0.400 ± 0.033 respectively. This still indicates an unexpectedly high $^3SO_2$ production rate in $^1SO_2$–$cis\text{-}C_4H_8$ collisions and a possible role of $^1SO_2$ in the photosensitized isomerization cannot be entirely dismissed on the basis of the present results.

The participation of additional non-emitting excited states of SO₂ in the photochemical reactions of SO₂ excited in the first allowed absorption region has recently been suggested by Cehelnik et al. to explain the quantum yields for CO₂ formation in the 313 nm photolysis of SO₂–CO mixtures[12]. CO₂ formation is believed to result from reactions of a non-emitting singlet (SO₂*) and a triplet (SO₂**) with little or no contribution from the optically active $^1SO_2$ and $^3SO_2$ states. Calvert and coworkers[11] have also studied the SO₂–CO system and find that an additional excited state (or isomer) of SO₂ is required to explain the data. They propose, however, that CO₂ formation only results from reactions of $^1SO_2$ and $^3SO_2$ and that the role of the new excited state is to provide an additional source of $^3SO_2$ molecules which increases with pressure. On this basis the triplet SO₂ production rates determined at low total pressures (such as have been used in emission studies) might be expected to be lower than those determined at higher pressures.
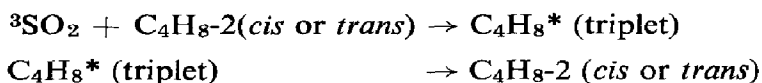
The unexpectedly high isomerization rates at low $[SO_2]/[cis\text{-}C_4H_8]$ ratios may also be attributed to the participation of an additional excited state either by enhanced $^3SO_2$ formation or by a direct reaction with butene-2 leading to isomerization. Further work including a study of the effect of total pressure on Φ_T and also an independent determination of the $^1SO_2$ quenching rate constants for the butene-2 isomers is necessary in order to elucidate the isomerization mechanism at low $[SO_2]/[cis\text{-}C_4H_8]$ ratios.

The data at high $[SO_2]/[C_4H_8]$ ratios are entirely consistent with the proposed mechanism involving the rapid addition of $^3SO_2$ molecules to butene-2 to give a diradical. The following decay processes of the diradical may be formulated:
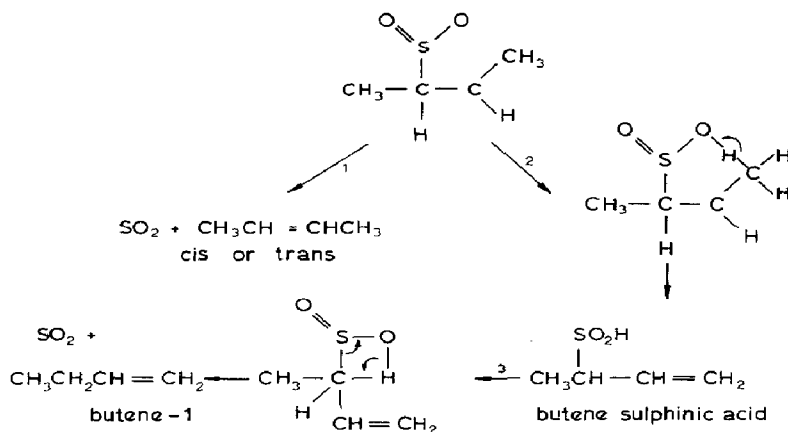
From the observed quantum yields for isomerization, sulphinic acid and butene-1 formation, the relative rates of processes (1), (2), (3) are $1:0.068:0.0014$ respectively. These are entirely consistent with the proposed reactions when the stereochemistry of the rearrangements are taken into account.

The alternative description given by Cundall and Palmer[3] for the isomerization reaction is triplet energy transfer from $^3SO_2$ to butene-2:

$^3SO_2 + C_4H_8$-2(*cis* or *trans*) $\rightarrow C_4H_8{}^*$ (triplet)

$C_4H_8{}^*$ (triplet) $\rightarrow C_4H_8$-2 (*cis* or *trans*)

The gas phase *cis–trans* isomerization of butene-2 in the presence of a number of photosensitizers (*e.g.* $Hg6{}^3P_1$, benzene, pyridine etc.) can best be interpreted in terms of a triplet energy transfer reaction yielding an olefin triplet which gives either the *cis* or *trans* isomer with equal probability upon deactivation[13]. With $^3SO_2$ the probability of formation of the *trans* isomer was greater than for the *cis* isomer. This may reflect the smaller amount of energy carried by $^3SO_2$ (73.7 kcal mol^{-1}) compared with the other sensitizers ($Hg6{}^3P_1 = 112.2$ kcal; benzene and pyridine $= 85$ kcal), a factor which is known to influence the photostationary composition in photosensitized isomerizations in the liquid phase[13]. On the other hand, the higher probability of *trans* isomer formation may result from the formation of a $C_4H_8SO_2$ diradical as suggested by Sidebottom *et al.* It is, however, very difficult to distinguish between energy transfer and reversible radical addition and further speculation regarding the detailed $^3SO_2$–olefin interaction is not justified on the basis of the present results.

The present study has demonstrated that the SO_2 photosensitized isomerization of *cis* (or *trans*) butene-2 provides a convenient method for the determination of the $^3SO_2$ yields in SO_2 photolysis systems in the first allowed absorption region. As indicated above, recent evidence suggests that the yield of $^3SO_2$ in these systems depends on both the nature of the gases present and on the total pressure. The $^3SO_2$ yield in the presence of the atmospheric gases at pressures of 1 atm is of particular interest since this will determine the photochemical reactivity of SO_2 in the atmosphere. It is proposed to extend the present study to obtain this information.

REFERENCES

1 G. M. Bristow and F. S. Dainton, *Proc. Roy. Soc.*, A229 (1955) 525.
2 F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, 46 (1950) 374, 382.
3 R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, 56 (1960) 1211.
4 H. W. Sidebottom, C. C. Badcock, J. G. Calvert, B. R. Rabe and E. K. Damon, *J. Am. Chem. Soc.*, 93 (1971) 3121.
5 J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*, Wiley, New York, 1966.
6 (a) H. D. Mettee, *J. Chem. Phys.*, 49 (1968) 1784; *J. Phys. Chem.*, 73 (1969) 1971.
  (b) S. J. Strickler and D. B. Howell, *J. Chem. Phys.*, 49 (1968) 1947.
  (c) T. N. Rao, S. S. Collier and J. G. Calvert, *J. Am. Chem. Soc.*, 91 (1969) 1609, 1616.
7 A. Horowitz and J. G. Calvert, *Int. J. Chem. Kinet.*, 4 (1972) 175, 191.
8 T. N. Rao and J. G. Calvert, *J. Phys. Chem.*, 74 (1970) 681.
9 H. W. Sidebottom, C. C. Badcock, J. G. Calvert, G. W. Reinhardt, B. R. Rabe and E. K. Damon, *J. Am. Chem. Soc.*, 93 (1971) 2587.
10 R. A. Cox, *J. Phys. Chem.*, 76 (1972) 814.
11 F. B. Wampler, A. Horowitz and J. G. Calvert, *J. Am. Chem. Soc.*, 94 (1972) 5523.
12 E. Cehelnik, C. W. Spicer and J. Heicklen, *J. Am. Chem. Soc.*, 93 (1971) 5371.
13 R. B. Cundall, in G. Porter, (ed.) *Progress in Reaction Kinetics*, Vol. 2, Pergamon Press, Oxford, 1964, p. 208.