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THE PHOTOLYSIS OF SO_2 AT 3130 Å IN THE PRESENCE OF THE 1,3-PENTADIENES*

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Summary

The photolysis of sulfur dioxide at 3130 Å and 22 °C in the presence of *cis*- and *trans*-1,3-pentadiene has been investigated. Quantum yield measurements for the $SO_2(^3B_1)$ photosensitized isomerization of *cis*-1,3-pentadiene to the *trans* isomer have been made for a variation in the $[SO_2]/[cis-C_5H_8]$ ratio of 2.48 to 464. A kinetic analysis of these data indicates that the quenching rate constant at 22 °C for the removal of $SO_2(^3B_1)$ molecules is $(1.73 \pm 0.35) \times 10^{11}$ l mol^{-1} s^{-1}. Estimates for the collisionally induced intersystem crossing efficiency of $SO_2(^3B_1)$ formation from $SO_2(^1B_1)$ are 0.14 ± 0.02 and 0.14 ± 0.01 (two difference kinetic analyses) for $SO_2(\tilde{X}, {}^1A_1)$ collisions with $SO_2(^1B_1)$ and 0.62 ± 0.05 for *cis*-C_5H_8 collisions. The photostationary composition of isomers was determined by starting with mixtures of SO_2 and pure isomer, either *cis*- or *trans*-C_5H_8, and extrapolating the prolonged irradiations to infinite time. In both cases a photostationary composition of $[trans]/[cis] = 1.19 \pm 0.05$ was found.

Introduction

The photochemistry of SO_2 irradiated in the presence of various olefins has been investigated recently by various workers [1 - 10]. These studies indicate that the $SO_2(^3B_1)$ molecule can photosensitize the isomerization of the 2-butenes [1 - 4], 2-pentenes [9, 10], 1,2-dichloroethylenes [5], and the 1,2-difluoroethylenes [6, 7]. The $SO_2(^3B_1)$ molecule seems to be the only active photosensitizer when the initial absorption act is $SO_2(^3B_1) \leftarrow SO_2(\tilde{X}, {}^1A_1)$. Also for total reaction pressures below about 50 Torr the $SO_2(^3B_1)$ state can successfully explain the observed photosensitized iso-

merizations of the olefins even when the initial absorption act is to the $SO_2(^1B_1)$ state.

The gas phase kinetics of the benzaldehyde photosensitized isomerization of the 1,3-pentadienes has been studied by DeMare' et al. [11]. Hammond et al. [12], have determined the photostationary composition of these isomers for photosensitizers of varying triplet energy in the liquid phase. Other work by Daubendiek and McMillan [13] indicates that even though cis-1,3-pentadiene is sensibly transparent in the spectral region $\lambda > 2800$ Å that there is a triplet—triplet energy transfer from surface states to gaseous 1,3-pentadiene which results in an isomerization. It seemed desirable to extend the work from this laboratory of SO_2/olefin systems to include a SO_2/diene system and the information already available from the above mentioned studies on the 1,3-pentadienes served to make these isomeric dienes a reasonable selection so that the results from the 1,3-pentadiene/SO_2 system could be compared with these earlier works. Accordingly, this study reports on results obtained from the 3130 Å photolysis of SO_2 in the presence of cis- and trans-1,3-pentadiene.

Experimental

The experimental apparatus has been described in detail in an earlier study [5] and only the essential features will be repeated here. A 1000 W Hg—Xe lamp was properly positioned in an Oriel Model 6140 housing and a focusing sleeve connected the housing to a 1/4 m Schoeffel GM-250 grating monochromator which employed a grating blazed at 4000 Å and had a reciprocal linear dispersion of 33 Å/mm slit width. The monochromator's spectral output was centered at 3130 Å and had a FWHM = 165 Å. Relative light intensities were measured using a 7020 Oriel radiometer unit utilizing a photodiode which had a spectral sensitivity maximum near 3400 Å. Absolute light intensity measurements were made using a Scientech Model 36-001 disc calorimeter in conjunction with a Scientech Model 362 power—energy meter. A cylindrical quartz reaction cell with a path length of 8.0 cm and a volume of 138 cm^3 was used for all photolyses.

Product analysis was performed using the flame ionization detection unit of a Model 810 Perkin-Elmer gas chromatograph. Separation of the isomers was achieved by using the following 1/8 in. diameter columns in series: (a) 24 ft. β,β-oxydipropionitrile (30%); (b) 24 ft. Silicon DC 550 (20%); (c) 24 ft. Silicon DC 550 (12%). The column temperature was maintained at 22 °C and the He flow rate was 40 cm^3/min for all analyses.

The vacuum system was an all Teflon stopcock-fitted system and was free of mercury and grease. Pressures were measured using Wallace—Tiernan gauges with ranges of 0 - 18, 0 - 75 and 0 - 380 Torr.

The cis- and trans-1,3-pentadiene were from Chemical Samples Company and each had a stated purity of 99.6% which was verified by gas chromatographic analysis. The isomers were transferred to storage bulbs on the vacuum

system, degassed at liquid nitrogen temperature, and used without further purification. Sulfur dioxide (Matheson anhydrous grade) was bulb-to-bulb distilled, degassed and the middle fraction was taken and used without further purification.

Results

Beer's law was followed for the pressures used and $\epsilon = 47.8$ l mol^{-1} cm^{-1} (base 10 units) was found for $\lambda = 3130$ Å, FWHM = 165 Å.

Photolysis of the isomers without SO_2 did result in photoisomerization even though the isomers are seemingly transparent in this spectral region. These observations support the earlier findings of Daubendiek and McMillan [13] that some gas—solid interface energy transfer mechanism may be occurring which permits adsorbed species to absorb the 3130 Å radiation and transfer the energy to gas phase 1,3-pentadiene molecules which can then undergo an isomerization. The isomerization rates for *trans* → *cis* and for *cis* → *trans* conversion without SO_2 present were determined to be about a factor of 200 less than the rate with SO_2 present. The exact relative rates depend upon concentration ratios, but for all those runs reported here the isomerization rates without SO_2 are insignificant compared to those rates with SO_2 and consequently the direct isomerization rates may be neglected in evaluating quantum yields.

Mixtures of SO_2 and the 1,3-pentadienes were prepared and allowed to stand at 22 °C without 3130 Å radiation for periods of time which exceeded the photolysis times. There was no evidence of any reaction at 22 °C in these gaseous mixtures even though SO_2 + diene thermal reactions have been reported in the literature [14] for more forceable reaction conditions.

Table 1 lists initial quantum yield data for the SO_2 photosensitized isomerization of *cis*-C_5H_8 to *trans*-C_5H_8. Figure 1 shows the plot used to determine the photostationary composition of isomers. The equilibrium [*trans*]/[*cis*] ratio was approached from both sides. Experiments were performed with 15.0 Torr SO_2 and 0.219 Torr *cis*-1,3-pentadiene and with 15.0 Torr SO_2 and 0.219 Torr *trans*-1,3-pentadiene and both studies revealed a photostationary [*trans*]/[*cis*] ratio of 1.19 ± 0.05.

The SO_2 photosensitized isomerization experiments indicated that essentially all of the 1,3-pentadiene could be accounted for by the sum of the two isomers. No additional peaks other than the *cis*- or *trans*-1,3-pentadiene peaks were observed on the chromatograms.

Discussion

Several investigations of the SO_2 photosensitized isomerization of various olefins have been performed [1 - 7, 9, 10] and all of these olefins have triplet energy levels which lie above that of the 73.6 kcal/mol triplet

TABLE 1

Photosensitized isomerization quantum yields for *trans*-1,3-pentadiene formation at 3130 Å[a,b]

P_{SO_2} (Torr)	$P_{SO_2}/P_{cis\text{-}C_5H_8}$	Rate × 10^{-12} (molecule/cm^3 s)	I_a × 10^{-13} (molecule/cm^3 s)	Φ
3.50	2.48	4.46	2.52	0.177
3.50	4.95	3.46	2.49	0.139
5.10	9.92	3.74	3.54	0.106
5.10	14.7	3.40	3.54	0.0960
8.10	18.3	4.53	5.26	0.0861
5.10	23.1	2.87	3.49	0.0822
10.0	45.7	4.31	6.27	0.0687
10.0	45.7	4.20	6.27	0.0670
10.0	45.7	4.47	6.27	0.0713
10.0	105	3.83	6.27	0.0611
10.0	155	3.48	6.27	0.0555
10.0	243	3.18	6.27	0.0507
10.0	319	2.76	6.27	0.0440
10.0	383	2.36	6.10	0.0387
12.1	464	2.67	7.05	0.0379

[a]Experiments were performed at λ = 3130 Å , FWHM = 165 Å.
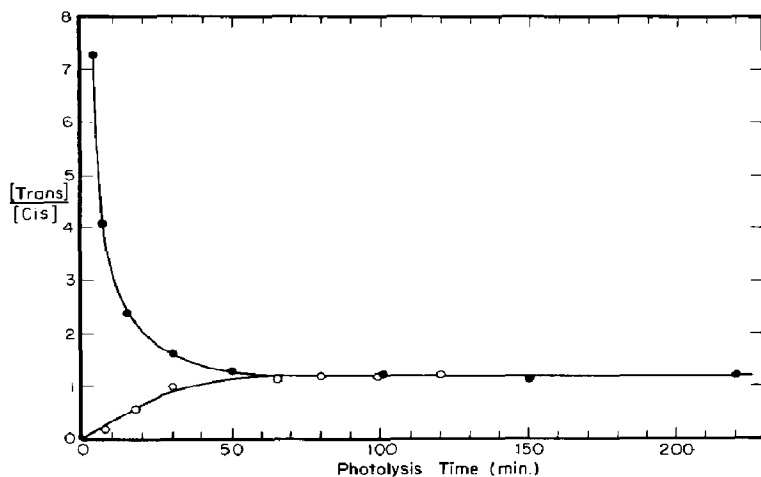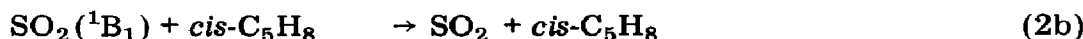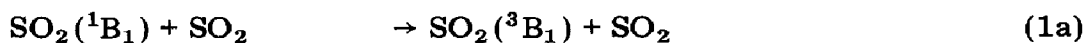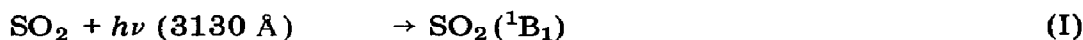[b]Temperature was 22 °C for all runs.

Fig. 1. Plot of the $[trans]/[cis]$ vs. the photolysis time. ○, $c \to t$ isomerization; ●, $t \to c$ isomerization. Initial reactant pressures were: $P_{cis\text{-}C_5H_8}$ = 0.219 Torr and P_{SO_2} = 15.0 Torr for *cis* study; $P_{trans\text{-}C_5H_8}$ = 0.219 Torr and P_{SO_2} = 15.0 Torr, *trans* study. Experiments were performed at 3130 Å and 22 °C.
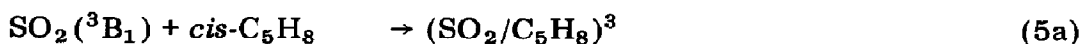
level of SO_2 ($^3B_1$) which has been noted to be the active photosensitizing spin state of SO_2. Thus, in these studies a direct triplet–triplet energy transfer from the sulfur dioxide triplet to the olefins would be endothermic. However, the triplet levels of *cis*- and *trans*-1,3-pentadiene lie at 57 kcal/mol [15] and

59 kcal/mol [15], respectively, and thus the energetics would be favorable for a triplet–triplet energy transfer from SO_2 ($^3B_1$) to either of the 1,3-pentadiene isomers. Recent studies on the quenching reactions of SO_2 ($^3B_1$) molecules by olefins [8, 16, 17] reveal that the magnitude of the quenching constant does not increase as the olefin's triplet level becomes lower. As Demerjian et al. [2] have noted, even though the triplet energy level for the chloroethylenes lie below that of ethylene, their quenching rate constants for removing SO_2 ($^3B_1$) molecules are less than that of ethylene itself. A recent study [8] from this laboratory showed that there is a very strong dependence of the magnitude of the quenching constant on the degree to which the olefin's π bond is polarized. The olefins which have less polarized π bonds have larger quenching rate constants for removing the excitation energy from SO_2 ($^3B_1$) molecules and the decrease in rate constant was pronounced for each member of the series C_3H_8, C_2H_4, C_2H_3F, $C_2H_2F_2$, C_2HF_3, C_2F_4, C_3F_6 changing from $(8.50 \pm 0.87) \times 10^{10} l\,mol^{-1}\,s^{-1}$ for C_3H_8 to $(0.0335 \pm 0.0027) \times 10^{10}\ l\,mol^{-1}\,s^{-1}$ for C_3F_6. This study was in agreement with earlier studies by Sidebottom et al. [16] and Wampler et al. [17] which favored the formation of a charge-transfer collision intermediate between SO_2 ($^3B_1$) and the olefinic quencher rather than a direct triplet–triplet energy transfer. In the study by Wampler et al. [17] the Arrhenius parameters for the quenching reaction of SO_2 ($^3B_1$) by olefinic quenchers revealed that the A factors were quite similar for different olefins but that the activation energies were larger as the degree to which the olefin's π bond was polarized became larger.

These observations on the removal of the electronic excitation energy from SO_2 ($^3B_1$) by olefins tends to support the quenching act proceeding via a $(SO_2/olefin)^3$ collision intermediate and diminishes the importance of a direct triplet–triplet energy transfer, although for the 1,3-pentadienes this latter possibility cannot be comfortably excluded. The mechanism presented below to account for the photolysis of SO_2 at 3130 Å in the presence of cis-1,3-pentadiene includes only the species $(SO_2/C_5H_8)^3$ although it is certainly possible that a triplet state of 1,3-pentadiene (Hammond's "phantom" triplet [12]) may be of importance. It is important to stress that the two species would be kinetically indistinguishable using the methods of the present investigation. Accordingly, the following mechanism which was successful at rationalizing the results of SO_2 photolyzed in the presence of the 2-butenes [3], 2-pentenes [10] and the 1,2-difluoroethylenes [6] for the $^1B_1 \leftarrow \tilde{X}, ^1A_1$ band of SO_2 is presented:

$$SO_2 + h\nu\ (3130\ \text{Å}) \qquad \rightarrow SO_2\,(^1B_1) \qquad\qquad\qquad\qquad (I)$$

$$SO_2\,(^1B_1) + SO_2 \qquad \rightarrow SO_2\,(^3B_1) + SO_2 \qquad\qquad (1a)$$

$$SO_2\,(^1B_1) + SO_2 \qquad \rightarrow 2SO_2 \qquad\qquad\qquad\qquad (1b)$$

$$SO_2\,(^1B_1) + \text{cis-}C_5H_8 \qquad \rightarrow SO_2\,(^3B_1) + SO_2 \qquad\qquad (2a)$$

$$SO_2\,(^1B_1) + \text{cis-}C_5H_8 \qquad \rightarrow SO_2 + \text{cis-}C_5H_8 \qquad\qquad (2b)$$

$$SO_2(^1B_1) + trans\text{-}C_5H_8 \quad \rightarrow SO_2(^3B_1) + SO_2 \tag{3a}$$

$$SO_2(^1B_1) + trans\text{-}C_5H_8 \quad \rightarrow SO_2 + trans\text{-}C_5H_8 \tag{3b}$$

$$SO_2(^3B_1) + SO_2 \quad \rightarrow SO_3 + SO(^3\Sigma^-) \tag{4a}$$

$$SO_2(^3B_1) + SO_2 \quad \rightarrow SO_2 + SO_2 \tag{4b}$$

$$SO_2(^3B_1) + cis\text{-}C_5H_8 \quad \rightarrow (SO_2/C_5H_8)^3 \tag{5a}$$

$$SO_2(^3B_1) + trans\text{-}C_5H_8 \quad \rightarrow (SO_2/C_5H_8)^3 \tag{5b}$$

$$(SO_2/C_5H_8)^3 \quad \rightarrow cis\text{-}C_5H_8 + SO_2 \tag{6a}$$

$$(SO_2/C_5H_8)^3 \quad \rightarrow trans\text{-}C_5H_8 + SO_2 \tag{6b}$$
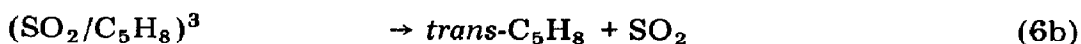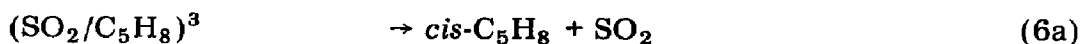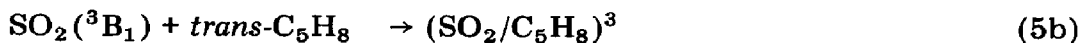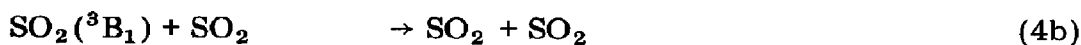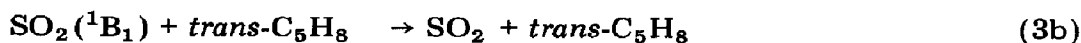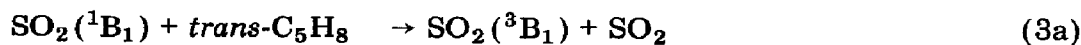
For the present experimental conditions the unimolecular decay of $SO_2(^1B_1)$ and $SO_2(^3B_1)$ are unimportant [18, 19]. The above mechanism suggests the following equation to explain the initial photosensitized quantum yields of cis- to trans-C_5H_8 formation with reactants cis-C_5H_8 and SO_2.

$$\Phi_{c \rightarrow t} = \frac{\dfrac{k_{6b}}{k_{6a} + k_{6b}} \left\{ \dfrac{k_{1a}}{k_{2a} + k_{2b}} \dfrac{[SO_2]}{[cis\text{-}C_5H_8]} + \dfrac{k_{2a}}{k_{2a} + k_{2b}} \right\}}{\left\{ 1 + \dfrac{(k_{1a} + k_{1b})[SO_2]}{(k_{2a} + k_{2b})[cis\text{-}C_5H_8]} \right\} \left\{ 1 + \dfrac{(k_{4a} + k_{4b})[SO_2]}{k_{5a}[cis\text{-}C_5H_8]} \right\}} \tag{A}$$

Equation (A) can be put into a more useful form if one makes some reasonable approximations. The study by Mettee [20] suggests that the quenching of $SO_2(^1B_1)$ molecules by various gases does not depend too strongly on the chemical complexity of the quencher. Calvert and Demerjian [3] have reported that $(k_{2a} + k_{2b})/(k_{1a} + k_{1b}) = 1.82$ when cis-2-butene is the collisional partner for $SO_2(^1B_1)$ molecules in reaction (2) above and if one assumes that this value does not change very much for cis-C_5H_8, at very high $[SO_2]/[cis\text{-}C_5H_8]$ ratios eqn. (A) reduces to (B):

$$\frac{1}{\Phi_{c \rightarrow t}} = \left(\frac{k_{6a} + k_{6b}}{k_{6b}} \right) \left(\frac{k_{1a} + k_{1b}}{k_{1a}} \right) \left\{ 1 + \frac{k_{4a} + k_{4b}}{k_{5a}} \frac{[SO_2]}{[cis\text{-}C_5H_8]} \right\} \tag{B}$$

Development of eqn. (B) also has assumed that at high $[SO_2]/[cis\text{-}C_5H_8]$ ratios most of the $SO_2(^3B_1)$ molecules produced via collisionally induced intersystem crossings will have been produced via collisions with SO_2.

A plot of the quantum yield data of Table 1 is given in Fig. 2 to test relationship (B). The plot shows a good linear fit at the higher $[SO_2]/[cis\text{-}C_5H_8]$ ratios and using those data points for $P_{SO_2}/P_{cis\text{-}C_5H_8} \geqslant 105$ a least squares treatment gives slope = 0.0298 ± 0.0051 and intercept = 13.2 ± 1.54 (95% confidence limits, twice the standard deviation). At the lower $[SO_2]/[cis\text{-}C_5H_8]$ points there is a pronounced curvature in the plot which indicates that the quantum yields are higher than those expected from extrapolation of the linear part of the plot. This implies that additional $SO_2(^3B_1)$ molecules, the active photosensitizer, are being produced by collisions of $SO_2(^1B_1)$ with cis-C_5H_8 at increasingly greater rates as the $[SO_2]/[cis\text{-}C_5H_8]$
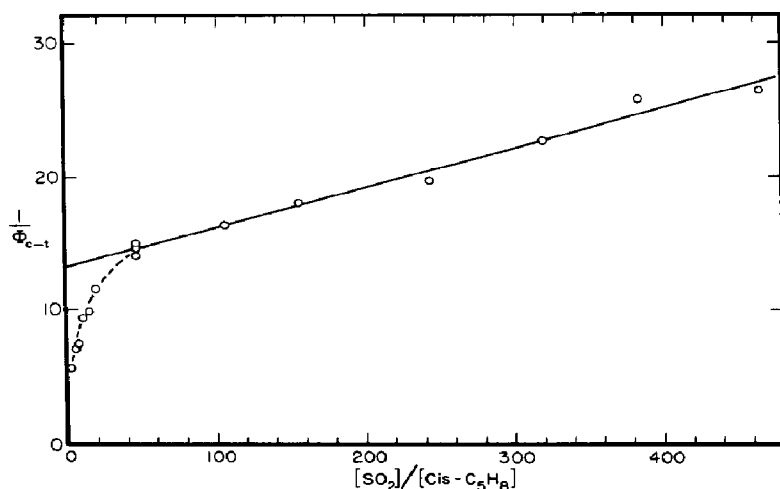
Fig. 2. Plot of $1/\Phi$ vs. the $[SO_2]/[cis\text{-}C_5H_8]$ ratio. Data taken from Table 1. Experiments were performed at 3130 A and 22 °C.

ratio decreases. Inspection of eqn. (B) reveals that the slope/intercept = $(k_{4a} + k_{4b})/k_{5a}$ and using the previously reported value [17, 18] of $k_{4a} + k_{4b} = (3.9 \pm 0.1) \times 10^8$ l mol^{-1} s^{-1} at 22 °C, k_{5a} is estimated to be $(1.73 \pm 0.35) \times 10^{11}$ l mol^{-1} s^{-1}. This is the first reported quenching rate constant for removal of $SO_2(^3B_1)$ by a diene and its magnitude implies that cis-1,3-pentadiene quenches $SO_2(^3B_1)$ very efficiently. A consideration of the photo-stationary composition of isomers predicted from the above mechanism yields:

$$\frac{[trans]}{[cis]} = \frac{k_{5a}}{k_{5b}} \frac{k_{6b}}{k_{6a}} \tag{C}$$

In those earlier studies where laser induced time resolved phosphorescence was employed to get very accurate values of quenching rate constants for removing $SO_2(^3B_1)$ molecules by cis- and $trans$-2-butene [2] and cis- and $trans$-1,2-dichloroethylene [5], it was found that within experimental error that no isomeric selectivity was noted for the rate constants. For cis- and $trans$-2-butene the values were $(1.29 \pm 0.18) \times 10^{11}$ and $(1.22 \pm 0.15) \times 10^{11}$ l mol^{-1} s^{-1}, respectively, and for cis- and $trans$-1,2-dichloroethylene the values were $(2.44 \pm 0.11) \times 10^{10}$ and $(2.59 \pm 0.09) \times 10^{10}$ l mol^{-1} s^{-1}, respectively. Thus, it seems reasonable that for cis- and $trans$-1,3-pentadiene that $k_{5a} \cong k_{5b}$ which implies that $[trans]/[cis] \cong k_{6b}/k_{6a}$ at the photostationary state. Using the value determined experimentally for the photostationary composition of isomers, $[trans]/[cis] = 1.19 \pm 0.05$ (Fig. 1) $k_{6b}/k_{6a} = 1.19 \pm 0.05$. Equation (B) predicts that Fig. 2 has intercept = $(k_{6a} + k_{6b})/k_{6b}$. $(k_{1a} + k_{1b})/k_{1a}$ and using the above mentioned values for k_{6b}/k_{6a} and the intercept, $k_{1a}/(k_{1a} + k_{1b})$ is found to be 0.14 ± 0.02. We will return to a discussion of $k_{1a}/(k_{1a} + k_{1b})$ later in the text.

Let us now return to eqn. (A) and attempt to fit all quantum yield data. If we use the results from the previous treatment at high $[SO_2]/[cis\text{-}C_5H_8]$
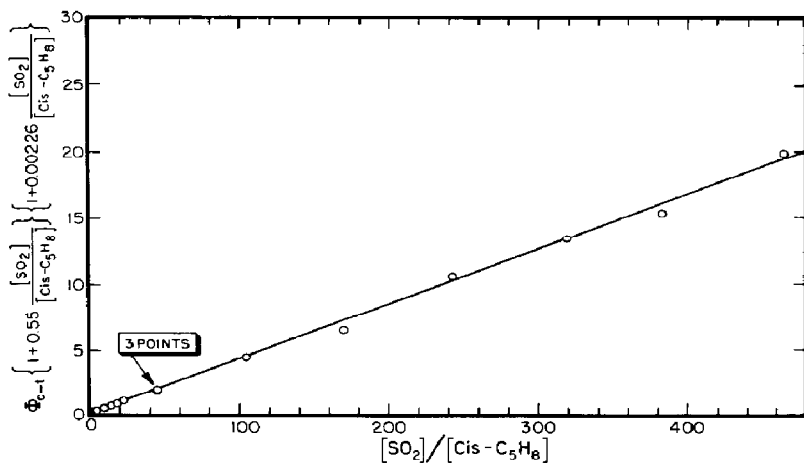
Fig. 3. Plot of the left hand side of eqn. (D) of the text $vs.$ the $[SO_2]/[cis\text{-}C_5H_8]$ ratio. Experiments were performed at 3130 Å and 22 °C.

ratio coupled with the estimate that $(k_{1a} + k_{1b})/(k_{2a} + k_{2b}) = 0.55$ [3] we have:

$$\Phi_{c \to t} \times \left\{ 1 + 0.55 \frac{[SO_2]}{[cis\text{-}C_5H_8]} \right\} \left\{ 1 + 0.00226 \frac{[SO_2]}{[cis\text{-}C_5H_8]} \right\}$$

$$= \left\{ \frac{k_{6b}}{k_{6a} + k_{6b}} \right\} \left\{ \frac{k_{1a} [SO_2]}{(k_{2a} + k_{2b}) [cis\text{-}C_5H_{10}]} + \frac{k_{2a}}{k_{2a} + k_{2b}} \right\} \tag{D}$$

Using all the data from Table 1 eqn. (D) is tested graphically in Fig. 3. There is an excellent linear fit for all data points and a least squares treatment gives slope = 0.0414 ± 0.0006 and intercept = 0.208 ± 0.125. Since the slope = $k_{6b}/(k_{6a} + k_{6b}) \times k_{1a}/(k_{2a} + k_{2b})$ and if we use previously mentioned rate constants, $k_{1a}/(k_{2a} + k_{2b}) = 0.0762 ± 0.0020$ results. Noting that $k_{1a}/(k_{2a} + k_{2b}) = [k_{1a}/(k_{1a} + k_{1b})]/[(k_{2a} + k_{2b})/(k_{1a} + k_{1b})]$ and using the estimate that $(k_{2a} + k_{2b})/(k_{1a} + k_{1b}) = 1.82$, $k_{1a}/(k_{1a} + k_{1b}) = 0.14 ± 0.01$ results. Other estimates of $k_{1a}/(k_{1a} + k_{1b})$ at 3130 Å that have been reported are 0.12 ± 0.01 [10], 0.12 ± 0.02 [10], 0.20 ± 0.05 [10], 0.20 ± 0.04 [10], 0.21 ± 0.04 [3], and 0.10 ± 0.01 [1, 3]. Thus, the present estimates of 0.14 ± 0.02 and 0.14 ± 0.01 fall within the range of previously reported estimates for the SO_2 collisionally induced intersystem crossing ratio in $SO_2(^1B_1)$. Although the spread of estimates for $k_{1a}/(k_{1a} + k_{1b})$ is over an unsatisfying large range the accuracy limitation imposed by use of intercept values in this study and others hopefully may be diminished somewhat by taking an average of all reported estimates and this gives $k_{1a}/(k_{1a} + k_{1b}) = 0.15 ± 0.06$.

The best estimate of the intercept can be made by using those points at low $[SO_2]/[cis\text{-}C_5H_8]$ values. Using only those values of $[SO_2]/[cis\text{-}C_5H_8] \leqslant 23.1$ an intercept = 0.336 ± 0.024 results. Since the intercept defined by eqn. (D) is given by $[k_{6b}/(k_{6a} + k_{6b})] [k_{2a}/(k_{2a} + k_{2b})]$ and if we use the

TABLE 2

Summary of rate constants

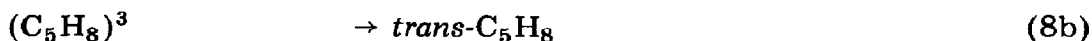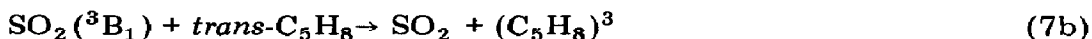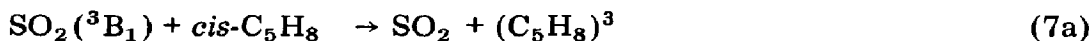| Rate constant	Value
$k_{1a}/(k_{1a} + k_{1b})$	0.14 ± 0.02
	0.14 ± 0.01
k_{6b}/k_{6a}	1.19 ± 0.05
$k_{2a}/(k_{2a} + k_{2b})$	0.62 ± 0.05
$k_{1a}/(k_{2a} + k_{2b})$	0.0762 ± 0.0020
k_{5a}	$(1.73 \pm 0.35) \times 10^{11}$ $l\ mol^{-1}\ s^{-1}$

TABLE 3

Experimental and calculated quantum yields[a]

$[SO_2]/[cis\text{-}C_5H_8]$	$\Phi_{calc.}$	$\Phi_{exp.}$
2.48	0.184	0.177
4.95	0.144	0.139
9.92	0.113	0.106
14.7	0.100	0.0960
18.3	0.0948	0.0861
23.1	0.0896	0.0822
45.7	0.0774	0.0687
45.7	0.0774	0.0670
45.7	0.0774	0.0713
105	0.0644	0.0611
155	0.0582	0.0555
243	0.0498	0.0507
319	0.0444	0.0440
383	0.0410	0.0387
464	0.0371	0.0379

[a]Calculated quantum yields are from eqn. (D) of the text.

known value of $k_{6b}/(k_{6a} + k_{6b})$, $k_{2a}/(k_{2a} + k_{2b})$ may be estimated by 0.62 $\pm$ 0.05. This rate constant ratio implies that cis-C_5H_8 is much more efficient than SO_2 in causing $SO_2(^1B_1)$ to be converted to $SO_2(^3B_1)$. Estimates of this intersystem crossing efficiency at 3130 Å for cis-2-pentene, $trans$-2-pentene, and cis-2-butene have been reported to be 0.51 ± 0.10 [10], 0.62 ± 0.12 [10] and 0.85 ± 0.38 [3] respectively. Thus, it appears that the fraction of collisions which a given collisional partner suffers with $SO_2(^1B_1)$ which are successful in inducing an intersystem crossing is dependent upon the chemical complexity of the collisional partner. Table 2 lists a summary of rate constants determined in this study.

It is instructive to see how self-consistent the quantum yield data are to the mechanism choice. Using the rate constants determined from Fig. 3, eqn. (D) was used to calculate quantum yields, $\Phi_{c \rightarrow t}$, for each $[SO_2]/[cis$-$C_5H_8]$ and the results are given in Table 3. There is an excellent fit between experimental and calculated quantum yields which is satisfying in that the mechanism choice and data are self-consistent. This does not, of course, eliminate other mechanisms, but it does lend support to the present choice.

Let us now direct more attention to the photostationary composition of isomers. The photostationary value, $[trans]/[cis] = 1.19 \pm 0.05$, determined is this study compares closely with an average value of 1.22 ± 0.05 determined by Hammond $et\ al.$ [12] for triplet energy sensitizers having a triplet energy of 62 - 75 kcal/mol. This leads one to speculate that perhaps the same excited state which decays to yield cis- and $trans$-1,3-pentadiene may be involved in both studies. This would involve the following reactions for the SO_2/C_5H_8 system:

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$$SO_2(^3B_1) + \textit{cis-}C_5H_8 \rightarrow SO_2 + (C_5H_8)^3 \tag{7a}$$

$$SO_2(^3B_1) + \textit{trans-}C_5H_8 \rightarrow SO_2 + (C_5H_8)^3 \tag{7b}$$

$$(C_5H_8)^3 \rightarrow \textit{cis-}C_5H_8 \tag{8a}$$

$$(C_5H_8)^3 \rightarrow \textit{trans-}C_5H_8 \tag{8b}$$

$(C_5H_8)^3$ is the Hammond "phantom" triplet which is the common triplet intermediate of reactions (7a) and (7b). These reactions could be occurring rather than reactions (5a), (5b), (6a), and (6b). However, this mechanistic difference would lend itself to a similar kinetic analysis as that treated in the text.

De Mare' *et al.* [11] have reported a photostationary composition, [*trans*]/[*cis*] = 1.38 ± 0.05 for the gas phase benzaldehyde photosensitized isomerization of the 1,3-pentadienes at 50 °C. The triplet level of benzaldehyde lies at 71.9 kcal/mol and the photostationary composition of isomers from their study is not too different from that of the present investigation. Their photostationary composition values is essentially equal to the natural decay ratio of the intermediate triplet and does lend some additional support that the same triplet may be involved in their study as in the SO_2/1,3-pentadiene system.

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