

THE ISOMERIZATION OF *CIS*-BUTENE-2 PHOTSENSITIZED BY SULPHUR DIOXIDE

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Summary

The SO₂ photosensitized ($\lambda > 3000 \text{ \AA}$) isomerization of *cis*-butene-2 was investigated at total pressures higher than 30 Torr. The results indicate that, contrary to observations at lower total pressures, the isomerization quantum yield is almost independent of the *cis*-butene-2/SO₂ ratio in the range 10⁻³ - 3.5. The "anomalously" high isomerization quantum yield suggests that the isomerization is induced mainly by some excited state of SO₂ other than the emitting (³B₁) triplet state, consistent with earlier observations of Cox and Demerjian.

Introduction

The investigation of the photoreaction of SO₂ with olefinic hydrocarbons is of special interest, since it is known that the latter enhance the formation of aerosols in SO₂ polluted atmospheres [1] and delay its photooxidation [2]. Up to now the information available on the mechanism and rates of these reactions is meagre. Additionally, the assignment of the reactive intermediate(s) is still a controversial matter.

Sulphur dioxide catalyzes the isomerization of butene-2 in a dark reaction, but the reaction is of negligible importance at room temperature [3]. The SO₂ photosensitized isomerization of *cis*-butene-2 in the gas phase was first investigated by Cundall and Palmer [4]. They irradiated with the full Hg arc and observed, besides the *cis-trans* isomerization, the formation of butene-1 together with small amounts of a substance postulated to be a butene sulphinic acid. Penzhorn and Güsten [5] showed that whereas NO strongly inhibits the isomerization, O₂ is 330 times less efficient. Recently Cox [6] and Demerjian [7] further investigated the SO₂ photosensitized isomerization of *cis*- (cC₄) and *trans*-butene-2 (tC₄). Using relatively low total reactant pressures, they observed a linear relationship between the isomerization quantum yield (Φ_{IC_4}) and the butene/SO₂ ratio. At high butene/SO₂ ratios (Cox) and at high CO₂ pressures (Demerjian) the Φ_{IC_4} was found to be unexpectedly large. While Cox pointed out that singlet excited SO₂ participation could not be excluded on the basis of his

results, Demerjian suggested the participation of another reactive unidentified species populated through collisionally induced intersystem crossing from a singlet excited state. The quite markedly different Φ_{tC_4} values measured in these investigations moved us to re-examine the isomerization in the SO_2/cis -butene-2 system under somewhat different experimental conditions.

Experimental

The experimental details have been described in a previous publication [5]. The radiation source was a 200 W HBO Osram lamp in conjunction with a Schott-Mainz 3150 Å interference filter. The light transmitted from the rear of the cell was measured with a photodiode. Actinometry measurements were conducted periodically and for each SO_2 pressure used, using highly purified NO_2 . In each case the fraction of light absorbed by SO_2 was exactly matched to that of the NO_2 actinometer and thus cumbersome corrections for light losses were avoided [8]. The extinction coefficient for NO_2 under our wavelength conditions was determined to be $69.5 M^{-1} cm^{-1}$, in good agreement with reported values [9]. The rate of formation of O_2 from the photolysis of NO_2 was measured with a Toepler pump, separating O_2 from NO with a solid N_2 trap. The oxygen quantum yield was taken to be 0.97 [10]. The measured light intensity was generally about 1.5×10^{15} quanta/s.

Results and Discussion

The results obtained from the irradiation of mixtures of SO_2 with *cis*-butene-2 at 23 °C have been summarized in Table 1. As the conversion was kept below 10% no correction for the *trans*-*cis* reaction was performed. From a few experiments, in which the rate of isomerization was measured simultaneously with the pressure drop, it was estimated that physical is at least 20 times more efficient than chemical quenching. Thus no correction was applied to possible *cis*-butene-2 removal owing to product formation. During some experiments it was observed that isomerization continued even in the absence of light. The cause of this behaviour is not clear. However, the addition of N_2 up to a constant total pressure of 665 mbar after the photolysis suppressed this effect and improved considerably the g.c. reproducibility. All experiments reported in this work were carried out under these conditions. From Table 1 it is apparent that the cC_4/SO_2 ratio, varied from 10^{-3} up to 3.46, has little effect on the isomerization quantum yield. Moreover, our results show that the isomerization quantum yields are independent of the SO_2 pressures.

Based on the work of Horowitz and Calvert [11] and Cehelnik *et al.* [12], the following simplified reaction scheme can be postulated to explain the results



TABLE 1

Rate of isomerization (R_{tC_4}) and quantum yields (Φ_{tC_4}) from the SO_2 photosensitized isomerization of *cis*-butene-2 at 3150 Å and room temperature

SO_2 (mbar)	cC_4 (mbar)	cC_4/SO_2	$R_{tC_4} \times 10^9$ ($M s^{-1}$)	$I_a \times 10^9$ (Einstein $l^{-1} s^{-1}$)	Φ_{tC_4}
18.62	64.51	3.46	1.63	4.70	0.35
33.25	97.76	2.94	1.86	5.85	0.32
32.85	76.87	2.34	2.03	5.89	0.35
33.25	76.48	2.30	1.99	5.89	0.34
18.62	38.57	2.07	1.63	4.90	0.33
32.19	69.16	2.15	1.69	5.98	0.28
18.62	21.28	1.14	1.19	4.70	0.25
32.59	31.92	0.98	2.42	7.13	0.34
32.59	31.52	0.97	2.62	7.05	0.37
33.25	29.93	0.90	2.29	7.00	0.33
64.51	57.86	0.90	2.30	5.93	0.39
66.50	55.86	0.84	2.79	6.35	0.44
18.62	12.64	0.68	1.28	4.74	0.27
63.84	33.25	0.52	2.11	6.06	0.35
33.12	16.09	0.49	1.97	7.71	0.26
33.25	13.97	0.42	1.83	7.29	0.25
32.85	13.70	0.42	1.99	7.13	0.28
67.17	17.96	0.27	1.89	6.35	0.30
33.92	6.78	0.20	1.55	7.46	0.21
64.51	9.04	0.14	1.70	6.59	0.26
166.25	12.5	0.08	2.10	9.02	0.23
159.60	5.99	0.04	2.13	9.27	0.23
159.60	3.72	0.02	2.13	9.27	0.23
159.60	1.73	0.01	1.77	9.31	0.23
359.1	1.33	0.0040	2.61	10.01	0.26
558.6	1.33	0.0024	2.67	9.11	0.29
552.0	0.80	0.0015	2.47	9.19	0.27
565.3	0.40	0.0008	1.22	9.48	0.13



where M stands for SO₂ plus cC₄, C₄SO₂ is the intermediate species leading to isomerization and SO₂^{*} and SO₂^{**} represent some as yet unidentified non-emitting singlet and triplet excited states of SO₂ that account for the "excess triplet SO₂" observed at high pressures [12, 13]. Several assumptions seemed appropriate to arrive at mechanisms (1) - (11): (i) all unimolecular photophysical processes are negligible at the pressures employed in this work [14, 15]; (ii) the collision induced intersystem crossing ratios of singlet SO₂ with SO₂ and cC₄ are comparable. Unfortunately data pertaining to the intersystem crossing ratio with cC₄ are not available in the literature; however, the recent findings of Horowitz and Calvert [16] reveal that this ratio is relatively insensitive to the nature of the collision partner; (iii) chemical self-quenching of ³SO₂ and SO₂^{**} is relatively unimportant [17, 18]; and (iv) collisions of ³SO₂ and SO₂^{**} with cC₄ will essentially lead, through some intermediate state, to isomerization. From steady state considerations the equation:

$$\Phi_{tC_4} = \left(\frac{k_{11}}{k_{10} + k_{11}} \right) \left(\frac{k_6 cC_4 k_1}{k_6 cC_4 + k_7 SO_2} + \frac{k_8 cC_4 k_3}{k_8 cC_4 + k_9 SO_2} \frac{k_4 M}{k_5 + k_4 M} \right) B \quad (I)$$

can be derived, where $B = (k_1 + k_2 + k_3)^{-1}$; the first term in eqn. (I) represents the contribution to the isomerization quantum yield from the phosphorescent excited triplet state (³SO₂) and the second that from the "excess" non-emitting triplet state (SO₂^{**}). (Cehelnik *et al.* [12] identified the SO₂^{**} with the ³A₂ state and James *et al.* [19] recently provided significant new evidence that substantiates this suggestion.)

Sidebottom *et al.* [20] have shown that $k_6/k_7 = 344$, thus $k_6 \cdot cC_4 > k_7 \cdot SO_2$ at $cC_4/SO_2 > 0.1$. If the assumption is made that the reaction of SO₂^{**} with butene is also very much faster than with SO₂ at $cC_4/SO_2 \geq 0.1$, it is expected that Φ_{tC_4} be a constant provided that $k_4 M > k_5$ at the pressures employed. An examination of the data from Table 1 indicates that this is indeed the case. From Table 1, at $cC_4/SO_2 \geq 0.68$ $\Phi_{tC_4} = 0.31 \pm 0.06$, which when combined with $k_{11}/(k_{10} + k_{11})$ as deduced from the photostationary *cis/trans* ratio of 0.33 [5] yields $(k_1 + k_3)/(k_1 + k_2 + k_3) = 0.41$. This value is considerably higher than that anticipated from phosphorescent studies at low pressures (*i.e.* 0.095 [13]). Our results for Φ_{tC_4} are, in the limit of high cC_4/SO_2 ratios and high pressures in reasonably good agreement with those of Cox [6] ($\Phi_{tC_4} > 0.2$) and those of Demerjian [7] ($\Phi_{tC_4} = 0.26$). As already observed by Demerjian, it appears that at high pressures about 40% of the collisions of excited singlet SO₂ lead to reactive triplet species. Provided the SO₂^{**} is not the phosphorescent triplet, as we require in our mechanism in contrast to the suggestion of Calvert and coworkers [11], the high pressure-high cC_4/SO_2 limit quantum yield of 0.31 suggests that the contribution to the isomerization of the SO₂^{**} far outweighs that from the ³SO₂ state.

In view of the demonstrated importance of total pressure on the kinetics of excited SO₂ reactions [13] it is not surprising to find substantial differences between the results of Demerjian (2 - 11 Torr) and Cox (~ 30 Torr) and those obtained in this work (160 - 500 Torr) at $cC_4/SO_2 < 1.0$

ratios. Whereas Demerjian and Cox observed a direct dependence of $(\Phi_{tC_4})^{-1}$ on the SO_2/cC_4 ratio (the measured quantum yields of Cox being generally about one half those of Demerjian's) at $SO_2/cC_4 > 1.0$, we were unable to find any significant dependency of the Φ_{tC_4} on SO_2/cC_4 . To account for this effect we require SO_2^{**} to be an excited state different from the 3SO_2 state and furthermore that $k_8/k_9 > k_6/k_7$. Should this be the case, then eqn. (I) may be rearranged to give:

$$[\Phi(SO_2^{**})]^{-1} = [\Phi_{tC_4} - \Phi({}^3SO_2)]^{-1} = (k_3 \cdot K)^{-1} \left(1 + \frac{k_5}{k_4 \cdot M} \right) \quad (II)$$

$$\Phi({}^3SO_2) = (k_1 K) \left(\frac{k_6 cC_4}{k_6 cC_4 + k_7 SO_2} \right) \quad (III)$$

where $K = k_{11}/(k_{10} + k_{11})(k_1 + k_2 + k_3)^{-1} \cdot \Phi({}^3SO_2)$ may be estimated, at known partial pressures of cC_4 and SO_2 , if $k_1 K$ is taken to be 0.015 and $k_6/k_7 = 344$. From a plot of $\Phi(SO_2^{**})^{-1}$ vs. M^{-1} with the data of Table 1 k_5/k_4 was estimated to be $3.5 \pm 1.5 \times 10^{-4} M^{-1}$ for $M = SO_2 + cC_4$. The reason for the large difference between this result and those obtained by Horowitz and Calvert [20] for CO_2 , CO and N_2 is at present not clear.

Since it is difficult to carry out a conclusive test of the possible mechanisms on the basis of the data presented we are at present re-examining this system with a view to determine in more detail the nature of the species involved in the isomerization.

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