Spectroscopic and Kinetic Studies of the SO Radical and the Photolysis of Thionyl Chloride

BY R. J. DONOVAN, D. HUSAIN AND P. T. JACKSON*

Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge

Received 17th April, 1969

The primary processes occurring in the photolysis of SOCl₂ have been examined using kinetic absorption spectroscopy in the ultra-violet and vacuum ultra-violet. Photodissociation involves the fission of one sulphur-chlorine bond, leaving an energized SOCl radical which may then undergo unimolecular decomposition to yield an SO radical and a further chlorine atom, or is stabilized by collision. The kinetics of the SO radical so formed are examined and a mechanism for removal is proposed. Two new electronic states of the SO radical are identified via new absorption systems in the vacuum ultra-violet designated SO($D^3\Pi \leftarrow X^3\Sigma^-$) and SO($E^3\Pi \leftarrow X^3\Sigma^-$). The D and E states are successive members of a Rydberg series and yield an approximate value for the first ionization potential of SO as 10.0 ± 0.1 eV. Molecular constants for the two states are given as

	$T_{00}(\text{cm}^{-1})$	$\Delta G'_{\frac{1}{2}}(\text{cm}^{-1})$	spin orbit coupling constant A $(\frac{1}{2}(^{3}\Pi_{2} ^{3}\Pi_{0}))$ (cm ⁻¹)
$SO(D^3\Pi)$	$54\ 259\pm30$	$1\ 254\pm20$	175 ± 10
$SO(E^3\Pi)$	67746 ± 45	1220 ± 20	187 ± 10

The extinction coefficient of the (7,0) band for the transition $SO(B^3\Sigma^- \leftarrow X^3\Sigma^-)$ is determined as $8.0 \pm 1.5 \times 10^6$ cm² mol⁻¹.

The kinetics of the reactions involving both the ground states and electronically excited states of O_2 ,¹ and S_2 ,² have received considerable attention; however, by comparison, quantitative data on the kinetics of the SO radical is more limited. This radical has been observed directly in a number of systems and by various techniques: Carrington *et al.*³ have reported observations on the e.p.r. spectrum of both ground state and the first singlet state of the SO radical, attributing its production to the energy transfer reaction,

$$O_2(a^1 \Delta g) + SO(X^3 \Sigma^-) \to SO(a^1 \Delta) + O_2(X^3 \Sigma \overline{g}).$$
(1)

Colin ⁴ has observed the second singlet state in emission via the transition $SO(b^{1}\Sigma^{+}\rightarrow X^{3}\Sigma^{-})$. However, little has been reported on the kinetics of these two excited states. Norrish and Oldershaw ⁵ have observed the $SO(B^{3}\Sigma^{-}\leftarrow X^{3}\Sigma^{-})$ system in the ultraviolet using kinetic spectroscopy, following the flash photodissociation of SO_{2} and SO_{3} . The kinetics of SO in these systems are discussed; however, it was not possible to derive quantitative kinetic data with their instrumentation. Thrush and Halstead ⁶ have used flow tube techniques to follow the intensity of the SO_{2} after glow and to monitor the rate of the termolecular recombination,

$$O + SO + M \rightarrow SO_2 + M. \tag{2}$$

Mass-spectrometric sampling techniques have also been employed to monitor the removal of SO following the reaction of oxygen atoms with carbonyl sulphide,⁷ and

* present address: Imperial Chemical Industries Ltd., Heavy Organic Chemicals Division, Billingham, Co. Durham.

results ⁸ derived from this method indicate that the rate for the bimolecular reaction between SO radicals is slow, in agreement with the findings of Thrush and Halstead.⁶ This technique ⁷ has also resulted in the detection of the metastable dimer, $(SO)_2$. In the present investigation we report the results of spectroscopic and kinetic experiments on SO by kinetic spectroscopy in the ultra-violet and vacuum ultra-violet. The extinction coefficient of the (7,0) band of the transition $SO(B^3\Sigma^- \leftarrow X^3\Sigma^-)$ is determined from measurements of the kinetic decay of this radical following the flash photolysis of SO_2 . The photolysis of thionyl chloride, which has received little attention,⁹ has been investigated and the kinetics of the SO radical described. Two new absorption systems of SO were observed in the vacuum ultra-violet and assigned to Rydberg transitions.

EXPERIMENTAL

The experimental arrangements for flash photolysis and kinetic spectroscopy in the vacuum ultra-violet and in the region of the ultra-violet close to the Schumann region, have been described previously.¹⁰ The concentrations of both stable and transient species were determined by plate photometry; adherence to the Beer-Lambert law being checked by the "two path" method ¹¹ for the transient species. Photometry of SO $(B^3\Sigma^- \leftarrow X^3\Sigma^-)$ was achieved via the intense bands at short wavelength associated with transitions from v'' = 0 to high vibrational levels of the upper state (v' = 7-16). A small, optically-fast spectrograph, Hilger model E 301, was used for observation in the wavelength region near 200 nm. Ignitron switching ¹² was employed in the discharge circuit for reliable and simultaneous firing of the two photoflash lamps in the apparatus. All experiments with SO₂ and SOCl₂ involved the addition of excess inert gas to prevent a significant rise in temperature on flashing, and all data are quoted for ~300 K.

A number of experiments employed optical filters to control the input of actinic light to the reactant system. This was achieved using a double-walled reaction vessel, the outer anulus of which being *ca*. 1 cm thick and containing a filter solution, and the inner comprising the reaction vessel. The transmission of these filter solutions and also the absorption spectrum of gaseous SOCl₂ were checked with a Unicam SP 800 recording spectrophotometer. The following solutions were employed : (1) saturated CuSO₄ solution; (2) 0.17 % weight/ volume KI solution; (3) 4N acetic acid solution; and (4) 1.5 % weight/volume KBr solution. These solutions transmitted light of wavelengths greater than 308.0, 254.0, 241.0 and 224.0 nm for the order presented. The filter solution (1) was employed to restrict the photolysis to Cl₂ only, when a mixture of Cl₂+SOCl₂ was flash-photolyzed. Filter solutions (2), (3) and (4) were used to limit the energy input above the OSCl—Cl bond dissociation energy and thus to test a mechanism involving the unimolecular decomposition of an energized SOCl molecule produced on photodissociation. Filters (2), (3) and (4) were changed after each flash.

MATERIALS

Ar ¹³, N₂ ¹³ and SF₆ ¹⁴ were employed as described previously. SO₂ (B.D.H. Laboratory Reagent) was trapped at liquid nitrogen temperature (-196° C), thoroughly degassed and fractionally distilled from room temperature to liquid nitrogen temperature. SOCl₂ (B.D.H. Laboratory Reagent) was thoroughly degassed and fractionally distilled from room temperature to liquid-nitrogen temperature.

RESULTS AND DISCUSSION

EXTINCTION COEFFICIENT OF SO($B^{3}\Sigma^{-} \leftarrow X^{3}\Sigma^{-}$) (7,0)

In order to facilitate a kinetic study of SO in the photolysis of thionyl chloride, it was found necessary to be able to measure the absolute concentration of this species. Thus the extinction coefficient of a band in the SO($B^3\Sigma^- \leftarrow X^3\Sigma^-$) system was measured. The basis of the method employed was the production of SO in the photolysis of SO₂

2932

KINETIC STUDIES OF SO RADICAL

where the kinetic decay of SO by processes, whose rate coefficients are established, may be compared with the time variation of the spectral intensity of the appropriate transition. The Franck-Condon factors associated with the electronic transition $SO(B^{3}\Sigma^{-} \leftarrow X^{3}\Sigma^{-})$ for the v'' = 0 progression are greater for the higher vibrational levels of the upper state.¹⁵ Whilst a number of transitions can be detected in this system, the (7,0) transition is most suitable for kinetic studies. A study at high resolution ⁴ of the B-X system has shown that although the (7,0) transition is strongly perturbed, it was not reported to be predissociated at low pressures. On the other hand, the (15,0) band is heavily predissociated and would, in general, be the more suitable transition for a determination of the extinction coefficient as it may be completely resolved at relative low optical resolution, thus yielding a first power dependence in the Beer-Lambert relationship. Unfortunately, this band was masked by the molecular spectrum of SO_2 . However, in experiments with $SOCl_2$, where both the (15,0) and (7,0) bands of the SO(B-X) system could be observed, both of these transitions gave rise to a first-power Beer-Lambert dependence. Thus, the high pressure of inert gas used in these experiments resulted in adequate broadening of the rotational fine structure such that the three band heads of the (7,0) transition overlap.⁴ However, rotational structure distant from the band heads will not contribute to the measured optical density with the resolution employed and the resulting extinction coefficient therefore represents a lower limit.

The photolysis of sulphur dioxide in the quartz ultra-violet ($\lambda > 185$ nm) yields ground-state species ⁵ according to the spin allowed process :

$$\mathrm{SO}_2(X^1A_1) + hv \to \mathrm{SO}(X^3\Sigma^-) + \mathrm{O}(2^3P_J). \tag{3}$$

The production of SO($a^1\Delta$), reported following e.p.r. spectroscopic observations in flow systems,³ and O¹D would not be thermochemically possible. Further, the kinetic spectroscopic observations following flash photolysis indicate that SO is formed predominantly in its ($X^3\Sigma^-$) ground state, there being no apparent delay in the build-up of the ground-state species which would be expected if this followed the relaxation of the metastable species SO($a^1\Delta$).

The removal of SO following the photolysis of SO_2 may occur by a number of processes :

L.

$$O + SO + M \xrightarrow{\kappa_2} SO_2 + M \tag{2}$$

$$SO + SO + M \rightarrow (SO)_2 + M$$
 (4)

$$SO + SO \rightarrow SO_2 + S$$
 (5)

$$(M+) S+SO \xrightarrow{\sim} S_2O.$$
 (6)

Reactions (4) and (5) are relatively slow as Thrush and Halstead ⁶ were unable to detect contributions from these reactions in their determination of k_2 using flow tube techniques $(k_2 = 3.2 \pm 0.4 \times 10^{17} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1})$. These authors give an upper limit for the second-order removal coefficient ((4) + (5)) of SO as $<4 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300 K. Although the formation of S_2O has been reported in the photolysis of SO₂,⁵ the concentration of this labile species was not determined and apparently reactions producing it are of minor importance. Nevertheless, the formation of S_2O requires that a fresh mixture of SO₂+inert gas be used for each flash-photo-chemical observation as the accumulation and secondary photolysis of such species would subsequently complicate the kinetics. Under the present conditions, the data of Thrush and Halstead ⁶ indicate that reaction (2) dominates the removal of SO.

The removal of oxygen atoms may occur via reaction (2) and also by the processes :

$$O + SO_2 + M \xrightarrow{k_7} SO_3 + M \tag{7}$$

$$O + SO_3 \rightarrow O_2 + SO_2 \tag{8}$$

$$O + O + M \xrightarrow{k_9} O_2 + M \tag{9}$$

$$O + O_2 + M \xrightarrow{h_1 O} O_3 + M$$
 (10)

$$O + O_3 \rightarrow 2O_2. \tag{11}$$

 k_7 has also been determined by Thrush and Halstead ⁶ and the contribution of reaction (7) will be negligible relative to that of (2) during the initial decay of SO under the conditions of these experiments, $(k_2/k_7 \simeq 70 \text{ for } M = \text{Ar at } 300 \text{ K}^6$; as $[\text{SO}_2] \simeq$ 10[SO], the initial rate of reaction (2) will be approximately 7 times greater than that of reaction (7)). Following Morgan and Schiff,¹⁶ $k_9 = 1.01 \times 10^{15} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ for $M = N_2$ and may be neglected together with (10) and (11) relative to (2) under the present conditions. Thus, the exceptionally high efficiency for reaction (2) allows a study of this reaction by monitoring the decay of SO by kinetic spectroscopy. N₂ was employed as a third body and would be expected to be characterized by an efficiency in reaction (2) similar to that for Ar (cf. analogous reaction involving NO ¹⁷).

From the foregoing, the decay of SO following the photolysis of SO₂ will be a second-order kinetic process, as observed, controlled by reaction (2). Following Halstead and Thrush ⁶ who report $k_2 = 3.2 \pm 0.4 \times 10^{17}$ cm⁶ mol⁻² s⁻¹ for M = Ar at 300 K, and relating the slope of the reciprocal of the optical density of the (7,0) (B-X) transition against time of observed magnitude 9.7×10^3 s⁻¹ at $p_{N_2} = 13.3$ kN m⁻² to the value of k_2 yields $\epsilon(7,0) = 8.0 \pm 1.5 \times 10^6$ cm² mol⁻¹. The γ value for sensitized Ilford HP3 plates at this wavelength was determined as 0.87 ± 0.13 . This result may be compared with the values of $\epsilon(12,0)$ (S₂ $B^3\Sigma_{\mu}^- \leftarrow X^3\Sigma_{g}^-$) of 1.1×10^7 and 3.9×10^6 cm² mol⁻¹ reported by Gaydon ¹⁸ and by Strausz and Gunning,¹⁹ respectively. The value of $\epsilon(7,0)$ for SO may now be used to estimate [SO]_{t=0} which compares favourably with a value obtained from a mass balance via the observed small depletion of the SO₂ spectrum in the region of 200 nm. Thus the assumption that reaction (2) controls the second-order decay of SO by virtue of the large size of k_2 [SO]/ k_7 [SO₂] is further justified.

PRIMARY PROCESSES IN THE PHOTOLYSIS OF THIONYL CHLORIDE

Continuous absorption by thionyl chloride in the ultra-violet commences at $\lambda \sim 290 \text{ nm}$. The extinction coefficient rises rapidly between 280-250 nm and thereafter, slowly to λ less than 200 nm. The available thermochemical data ²⁰ indicate that the energy required to rupture the two S—Cl bonds is ~4.8 eV, corresponding to a wavelength of $\lambda < 260.0 \text{ nm}$. On the isothermal flash-photolysis of SOCl₂ in the quartz ultra-violet, Cl($3^2P_{\frac{3}{2}}$) ($3p^44s(^2P_{\frac{3}{2}}) \leftarrow 3p^5(^2P_{\frac{3}{2}})$, 134.7 nm) is observed in absorption in the Schumann region together with two new groups of bands. The ($B^3\Sigma^- \leftarrow X^3\Sigma^-$) system of SO is readily seen in the ultra-violet principally via the v'' = 0 progression (fig. 1) but up to four vibrational quanta may be observed weakly in absorption under conditions where vibrational relaxation is slow. The new band systems in the vacuum ultra-violet are attributed to transitions from the ground state to the ($D^3\Pi$) and ($E^3\Pi$) states. The reduction in the continuum of SOCl₂ indicates that up to 75 % of the molecule may be photolyzed although it was generally

KINETIC STUDIES OF SO RADICAL

much lower than this and in kinetic experiments, it was chosen to be so. SO₂ and S₂O are observed at long delay together with the slow formation of a weak spectrum of $S_2(B^3\Sigma_u^- \leftarrow X^3\Sigma_g^-)$. The production of SO₂ is symmetrical with the decay of SO.

 $Cl(3^2P_{\frac{3}{2}})$ is produced directly in the primary photochemical act and does not result from the secondary photolysis of Cl_2 . Separate experiments on Cl_2 itself employing kinetic spectroscopy in the vacuum ultra-violet indicate that only a small fraction of this molecule is photolyzed, even at low partial pressures. Molecular chlorine from the photolysis of SOCl₂ is only observed at long delay and results from slow termolecular atomic recombination. Abstraction reactions such as

$$Cl + SOCl_2 \rightarrow Cl_2 + SOCl$$
 (12)

and

$$Cl + SOCl \rightarrow Cl_2 + SO$$
 (13)

thus do not account for the initial photochemical products. The absence of any significant contribution by the former of these processes is further evidenced by the lack of any reduction in the SOCl₂ continuum when Cl₂ alone was photolyzed (filter (1)), in mixtures of these two compounds; the concentration of Cl atoms so produced was large compared with that of SOCl₂. Further, although in exothermic meta-thetical reactions of atoms and polyatomic molecules, the "old" bond may be vibrationally excited,²¹ in most cases,²² excess vibrational energy appears in the newly formed bond. Thus reaction (13) would not be expected to yield the SO($v'' \leq 4$) observed here.

A comparison between the extent of the photolysis of $SOCl_2$, obtained by monitoring the continuum of this molecule, and the yield of SO obtained using the measured extinction coefficient for the (7,0) transition of the $SO(B \leftarrow X)$ system, reveals that [SO] accounts for only 10-20 % of the photolysis products and that some further intermediate must be produced to satisfy a mass balance. Whilst this is most probably the SOCl radical, no spectrum that could be attributed to this species was observed. This radical has apparently not been observed spectroscopically hitherto and it would thus appear from our examination that any spectrum associated with this species in the visible or the ultra-violet would be continuous. The secondary photolysis of SOCl to yield SO was negligible as the concentration of SO at a given time delay was a linear function of the flash intensity, indicating that a single photon process is involved in the production of this diatomic molecule (fig. 2).

Experiments were performed in order to ascertain whether an energized precursor SOCl* formed on the initial photochemical act, then decomposed unimolecularly to yield SO. The basis of such a mechanism may be written

$$SOCl_2 + hv \rightarrow SOCl^* + Cl \tag{14}$$

$$SOCI^* \rightarrow SO + CI$$
 (15)

$$SOCl^* + M \rightarrow SOCl + M.$$
 (16)

The competition between unimolecular decomposition and collisional deactivation results in a relationship analogous to a Stern-Volmer plot, namely, 1/[SO] against [M] being linear. This type of behaviour has been observed by Simons and Yarwood ²³ for the decomposition of energized halogenated methyl radicals. The unimolecular rate constant k_E at a given excitation energy E and critical energy E^* for breaking the appropriate bond is given by ²³

$$k_E = v(1 - E^*/E)^{n-1}$$
.

v is the rate constant when $E \ge E^*$ such that decomposition takes place in one vibration and n is the number of vibrational modes coupled with the critical mode for decom-





[To face page 2934.

Published on 01 January 1969. Downloaded by University of California - Santa Barbara on 14/09/2015 18:14:07.



2935

position, or the number of effective oscillators. The controlled input of excess energy above the dissociation energy of OSCl—Cl was achieved by means of optical filters allowing the three sets of experiments with ca. 0.09 (filter (2)), 0.34 (filter (3)) and 0.74 eV (filter (4)) of excess energy. Whilst the use of filters reduced the initial yield

FIG. 2.—Dependence of the intensity of the SO($B \leftarrow X$) (15,0) band (peak height h) as a function of flash energy E. $p_{\text{SOCl}_2} = 2.7 \text{ N m}^{-2}$; $p_{\text{Ar}} = 20.0 \text{ kN m}^{-2}$; delay = 20 µs.

of SO due to a reduction in the light absorbed by $SOCl_2$, it was still possible to observe a further reduction in the yield of this diatomic molecule with a given filter by increasing the added inert gas (N₂) pressure from 2.66 to 100.2 kN m⁻² although the results were not sensitive to such a change. With this range of pressure of inert gas and the excess energies in the order above, the yields of SO were reduced by factors of approximately 2 and 0.3 for the two lowest energies, respectively, but no effect was observed for the third. This effect is not as large as that obtained for the halogenated methyl radicals ²³ where the number of effective oscillators is greater, the life-time of the free radical is longer and thus the effect of inert gas and collisional deactivation more pronounced. Nevertheless, the observations satisfy the basis of the mechanism contained in (14), (15) and (16). Experiments with Ar and SF₆ as the inert gas showed that the former was only slightly less efficient than N₂ in reaction (16) while the latter was the same within the experimental limits.

KINETICS OF SO IN THE PHOTOLYSIS OF THIONYL CHLORIDE

The decay of SO following the photolysis of $SOCl_2$ was first order, plots of $log_{10}[SO]$ against time being linear over a ten-fold change in [SO] (fig. 3). Second- and third-order plots showed significant curvature. The first-order decay coefficient of SO is independent of the pressure of inert gas but increased linearly with the initial pressure of $SOCl_2$. However, no significant variation in the rate of decay could be

KINETIC STUDIES OF SO RADICAL

observed when the extent of photolysis was varied in the range 40-75 % by variation of the flash energy. Only 10-20 % of the photolysis products appears as SO and thus [SOCI]/[SO] ~4. Furthermore, the variation of [SOCI] with inert gas pressure will be small as the proportion of energized SOCI radicals capable of undergoing unimolecular decomposition is low and reaction (16) is relatively inefficient. Thus, the observed pseudo-first-order decay of SO, the first-power dependence on the initial concentration of SOCI₂, the independence from inert-gas pressure and the observed growth of SO₂, symmetrical with the decay of SO, strongly suggests that the reactions

$$SO + SOCl_2 \rightarrow SO_2 + SCl_2 \qquad \Delta H = -1.19 \text{ eV}, ^{20} \tag{17}$$

$$SO + SOCI \rightarrow SO_2 + SCI$$
 $\Delta H = -1.08 \text{ eV}, ^{20} (?)$ (18)

are involved. Variation of the extent of photolysis did not give rise to significant differences in the rates at which SO was removed which implies that both reactions are characterized by similar rate coefficients. The overall decay may therefore be described by $k_{17}+k_{18} = 7.4\pm2.5\times10^{11}$ cm³ mol⁻¹ s⁻¹.

FIG. 3.—The first-order decay of SO in the presence of SOCl₂. SO($B^{3}\Sigma^{-}\leftarrow X^{3}\Sigma^{-}$) (15,0) band monitored. $p_{Ar} = 20.0 \text{ kN m}^{-2}$; E = 2000 J. p_{SOCl_2} : \bigcirc , 2.1; \bigcirc , 4.4; \bigcirc , 10.0 N m⁻².

In view of the first-order kinetics observed for the removal of SO, it may be concluded that bimolecular reactions involving this radical are relatively slow in this system. However, the observation of S_2O and S_2 requires comment. It is generally considered that SO is the kinetic precursor of S_2O in systems containing these species, particularly in the oxidation of sulphur compounds.²⁴⁻²⁶ A group of reactions can be postulated which satisfies this and the slow production of S_2 observed in these experiments, viz.,

$$SO + SO \rightarrow SO_2 + S$$
 (5)

$$S + SO \rightarrow S_2O$$
 (6)

$$\mathbf{S} + \mathbf{S} + \mathbf{M} \to \mathbf{S}_2 + \mathbf{M} \tag{19}$$

An alternative scheme has been proposed by Schenck ⁷ following the observation of $(SO)_2^+$ in mass-spectrometric studies, viz.,

$$SO + SO \rightarrow (SO)_2$$
 (4)

$$SO + (SO)_2 \rightarrow SO_2 + S_2O. \tag{20}$$

2937

This scheme is not compatible with the observed production of S_2 in our experiments; however, the possibility that S_2 is produced via some reaction other than (19) cannot be entirely ruled out. It is difficult to assess quantitatively the significance of the observed yields of S_2O as the value of the extinction coefficient of this species is uncertain. Jones ²⁷ has reported that the extinction coefficient for the 260-340 nm system of this molecule is probably 10-100 times greater than that for SO_2 in the same region. However, we may conclude from the observed kinetics that $k_5 < 7 \times 10^{10}$ cm³ mol⁻¹ s⁻¹. This limit is significantly less than a previous value ²⁸ given for k_5 as 2.6×10^{12} cm³ mol⁻¹ s⁻¹ but is in agreement with the upper limit given by Thrush and Halstead ⁶ (<4 × 10⁹ cm³ mol⁻¹ s⁻¹) and by Wagner *et al.*⁸ (<10¹⁰ cm³ mol⁻¹ s⁻¹).

VACUUM ULTRA-VIOLET SPECTRUM OF SO

In addition to the atomic spectrum of $Cl(3^2P_{\frac{1}{2}})$ a number of strong, transient bands was observed in the vacuum ultra-violet (fig. 4, table 1) following the photolysis of thionyl chloride ($P_{SOCl_2} = 2.7 \text{ N m}^{-2}$; $P_{Ar} = 12 \text{ kN m}^{-2}$). The six bands in the region 184.3-178.9 nm have been reported previously during the slow oxidation of carbon disulphide and hydrogen sulphide, and when sulphur dioxide was adiabatically flash-heated.²⁹ The observation of this spectrum was related by McGrath *et al.*²⁹ to the appearance of the continuous absorption in the quartz ultra-violet which precedes the normal spectrum of SO₂ in the oxidation of some sulphur compounds,²⁴⁻²⁶ and which has been attributed to a thermal isomer of SO₂.²⁹ However, the observation of the transient bands (184.3-178.9 nm) in the vacuum ultra-violet in the region of room temperature in this investigation establishes that these are not due to a thermal isomer of SO₂.

Table 1.—Observed wavelengths for the SO radical in the vacuum ultraviolet together with those for the analogous transition of $S_{\rm 2}$

transition	v',v"	$\lambda_{obs} (vac)^{(nm)}$	$v_{obs}(cm^{-1})$
$S_2(D^3\Pi \leftarrow X^3\Sigma_g^-)^{30, 38}$		170.795	58 549.7
	0,0	170.237	58 741.5
		169.461	59 010.8
		168.532	59 335.9
	1,0	167.988	59 528.1
		167.234	59 796.3
$SO(D^3\Pi \leftarrow X^3\Sigma^-)$ *		184.30	54 259
	0,0	183.84	54 394
		183.20	54 586
		180.14	55 513
	1,0	179.63	55 670
		178.94	55 884
$SO(E^3\Pi \leftarrow X^3\Sigma^-)$		147.61	67 746
	0,0	147.23	67 921
		146.86	68 092
		145.00	68 9 66
	1,0	144.53	69 190
		144.16	69 367

* As these bands are diffuse, measurements were made from band centres and agree within the error for measurement with those reported by McGrath *et al.*²⁹

KINETIC STUDIES OF SO RADICAL

The formation and decay of this transient spectrum follows that of the established ultra-violet spectrum of $SO(B^{3}\Sigma^{-}\leftarrow X^{3}\Sigma^{-})^{4,5,29}$ in this system which strongly suggests that the carrier may be attributed to the SO radical. However, such kinetic evidence may be unreliable when taken in isolation. Thus, in addition, we here make a comparison with the spectrum of the analogous species, S₂. Unfortunately, a rotational analysis could not be attempted with the optical resolution available, and an assignment can thus only be made by examination of the vibrational and electronic term differences observed. Colin⁴ has observed the longer wavelength system under high resolution and reports it to be heavily predissociated, and thus a more detailed analysis than presented here may not be possible. The similarity of the long wavelength system to that of $S_2(D^3\Pi \leftarrow X^3\Sigma_a)$ is striking and both have been reproduced in fig. 5 from spectra taken under the same resolution. Further, a quantitative comparison may be made with the data for these two systems collected in tables 1 and 2. The bands of $S_2(D \leftarrow X)$ fall into two groups of three, the longer wavelength group arising from the (0,0) transition and the shorter wavelength group from the (1,0)transition.³⁰⁻³¹ The term differences between these two groups thus yields the upper state vibrational frequency, $\Delta G'_{\pm} = 786 \text{ cm}^{-1}$, indicating that the transition involves the promotion of an anti-bonding electron to a weakly bonding or non-bonding orbital.³¹ The upper state must thus be Rydberg in type.³¹ The spectrum now tentatively attributed to SO falls even more clearly into two groups of three bands, the separation between the groups being 1 254 cm⁻¹. This shows the expected relationship to the ground-state frequency of SO ($\Delta G_{*}^{\prime\prime} = 1.136.0 \text{ cm}^{-1}$) if the transition is Rydberg in type.

Table 2.—Molecular constants for some electronic states of SO compared with those for $S_{\rm 2}$

electronic state	$T_{00} (\mathrm{cm}^{-1})$	$\Delta G_{\frac{1}{2}}$ ³⁸ , ⁴	spin orbit coupling constant A $(\frac{1}{2}(^{3}\Pi_{2}-^{3}\Pi_{0}))$ (cm - 1)
SO $X^{3}\Sigma^{-}$		1 136.0	
SO $D^3\Pi$	54 259	1 254	175 *
SO $E^3\Pi$	67 746	1 220	187
$S_2 X^3 \Sigma_g^{-31}$		719.98	
$S_2 D^3 \Pi^{31}$	58 549.7	786	231

* The spin orbit coupling constant for the $A^{3}\Pi$ state of SO has been given as approximately 150 cm⁻¹.⁴

The ground electronic state of S_2 is $S_2(X^3\Sigma_g^-)$ and thus the structure of the $S_2(D \leftarrow X)$ transition has been interpreted on the basis that the upper state be designated $S_2(D^3\Pi)$.³⁰ Barrow ³¹ has tentatively assigned the upper state* as ${}^3\Pi_{g, r}$ associated with the electronic structure $(\sigma_g 3p)^2(\pi_u 3p)^4(\pi_g 3p)(\sigma_g 4s)$. Fig. 5 shows that the $S_2(D \leftarrow X)$ system is weaker than that of $S_2(C \leftarrow X)$ which is compatible with the former being partially forbidden by the $g \leftrightarrow g$ selection rule.³¹ (This selection rule will not hold for SO and the transition will be fully allowed.) The observed three band heads in each group of the systems $S_2(D^3\Pi \leftarrow X^3\Sigma_g^-)$ thus arise from transitions to the three spin orbit components of the upper state, viz., ${}^3\Pi_2$, ${}^3\Pi_1$ and ${}^3\Pi_0$. The splitting between these states allows a determination of the spin orbit coupling constant.³¹ This constant for the analogous state of SO should be smaller due to the presence of a lighter atom. A value has been reported for the $A^3\Pi$ state following a high-resolution analysis of the system $SO(A^3\Pi \leftarrow X^3\Sigma)$ by Colin.⁴ Our value (table 2) is in accord with that measurement.

* Note added in proof: Barrow et al. (R. F. Barrow and J. M. Ricks, J. Phys. B, 1969, 906) have now confirmed this assignment but suggest that the upper state be associated with the electronic structure... $\pi_g(\sigma_u 4p)$.

2939

A further intense system of SO, hitherto unreported, may be observed to shorter wavelength (fig. 4, table 1). The close similarity in structure with the system described above indicates that the upper state is again ${}^{3}\Pi$ and thus probably the second member of the Rydberg series with the upper state electronic configuration . . . $(\pi^{*}3p)$ (σns). Significant deviations from the Rydberg formula generally occur for the first member of such a series (owing to its close proximity to the valency shell orbitals, significant perturbations may occur). Thus, the two transitions observed will only allow a rough extrapolation to the ionization limit. We employ the relationship

$$v_n(\text{obs.}) = \text{ionization potential} - R/(n-\delta)^2,$$
 (i)

where v_n (obs.) is the observed frequency of the transition, R the Rydberg constant, n the principal quantum number of the Rydberg orbital (which must be ≥ 4 for s and p orbitals of SO, or ≥ 3 for d orbitals) and δ is the quantum defect. δ has values between 1.99-2.02 for the s orbitals of the free S(I) atom and between 2.04-2.05 for compounds of the type R—S—R, where R = H or CH_3^{32} ; a quantum defect of 2.1 has been given for a Rydberg series associated with the SH radical.³² Thus, for the proposed electronic configuration, substituting $\delta = 2.0$ and n = 4 and 5 in eqn (i) yields I.P.(SO) = 10.0 ± 0.1 eV. This would further predict that the next Rydberg transition had its origin at ~ 137 nm. Unfortunately, the plate density in this region is not adequate to allow precise measurements though there is some indication from our plates of transient bands in this region. The exact value for the ionization potential is very sensitive to the value chosen for δ . For excitation to p type orbitals, δ may be expected to take the value of 1.5 whilst for excitation to d type orbitals, $\delta = 0.4$. Thus, the assignment to a Rydberg series associated with ns orbitals gives rise to the highest value for the ionization potential calculated on this basis. Blanchard and Le Goff³³ have given the ionization potential of SO as 12.1 ± 0.3 eV. However, their treatment of the data gave $D(OS-O) = 4.0\pm0.30$ eV which is certainly incorrect. Recalculating using their data for

$$SO_2 \rightarrow SO^+ + O, \qquad \Delta H = 16.1 \pm 0.2 \text{ eV},$$
 (21)³³

and the more reliable value for

1

$$SO_2 \to SO + O, \qquad \Delta H = 5.61 \text{ eV},$$
 (22) ³⁴

yields the ionization potential of SO as 10.5 ± 0.2 eV, which is in more reasonable agreement with the value obtained here. The earlier data of Smyth and Meuller³⁵ using electron impact techniques gave a value for the thermochemistry of reaction (21) of 16 ± 0.5 eV which, with the value for (22) above, gives I.P. (SO) = 10.4 ± 0.5 eV. There is thus reasonable agreement between the value for the ionization potential of SO found here and the corrected data for the two other independent methods.

Further evidence for the assignment of the vacuum ultra-violet systems considered above to the SO radical would be provided if vibrationally excited levels of the ground state could be observed in absorption; however, attempts to observe these levels have not been successful. Additionally, the appearance of only two bands indicates that the potential curves lie almost symmetrically, one above the other. There is no obvious shading of the bands under the resolution used here. The analogous transitions of O_2 have not been reported and may lie beneath the strong continuum associated with the Schumann-Runge system. The first of these transitions for O_2 might lie in the region 110-130 nm ³⁶ where a number of discrete transitions have been observed; however, an analysis of several bands in this region ³⁷ has not lead to its identification.

We thank Prof. J. W. Linnett, F.R.S. for encouragement and laboratory facilities.

- ¹ M. A. A. Clyne, B. A. Thrush and R. P. Wayne, *Photochem. Photobiol.*, 1965, **4**, 957; T. P. J. Izod and R. P. Wayne, *Proc. Roy. Soc. A*, 1968, **308**, 81; J. Heicklen and T. Johnston, *J. Phys. Chem.*, 1967, **71**, 1391; S. J. Arnold, N. Finlayson and E. A. Ogryzlo, *J. Chem. Phys.*, 1966, **44**, 2529.
- ² O. P. Strausz, Organosulphur Chemistry, ed. M. J. Janssen (Interscience, London, 1967, p. 13); P. Fowles, M. de Sorgo, A. J. Yarwood, O. P. Strausz and H. E. Gunning, J. Amer. Chem. Soc., 1967, 89, 1352; O. P. Strausz, R. J. Donovan and M. de Sorgo, Ber. Bunsenges., 1968, 72, 253.
- ³ A. Carrington, D. H. Levy and T. A. Miller, Trans. Faraday Soc., 1966, 62, 2994.
- ⁴ R. Colin, Can. J. Phys., 1968, 46, 1539; R. Colin, Can. J. Phys., 1969, 47, 979.
- ⁵ R.G. W. Norrish and G. A. Oldershaw, Proc. Roy. Soc. A, 1959, 249, 498.
- ⁶ C. J. Halstead and B. A. Thrush, Proc. Roy. Soc. A, 1965, 295, 363.
- ⁷ P. W. Schenk, Angew. Chem. (inter. ed.), 1965, 4, no. 5, 402.
- ⁸ Von K. Hoyermann, H. Gg. Wagner and J. Wolfrum, Ber. Bunsenges., 1967, 71, 603.
- ⁹ R. Cherton, Bull. Soc. Roy. Sci. Liege, 1942, 11, 54.
- ¹⁰ R. J. Donovan, F. G. M. Hathorn and D. Husain, Trans. Faraday Soc., 1968, 64, 1228.
- ¹¹ R. G. W. Norrish, G. Porter and B. A. Thrush, Proc. Roy. Soc. A, 1953, 216, 165.
- ¹² I. M. Napier and R. G. W. Norrish, Proc. Roy. Soc. A, 1967, 299, 317.
- ¹³ R. J. Donovan and D. Husain, Trans. Faraday Soc., 1966, 62, 11.
- ¹⁴ R. J. Donovan and D. Husain, Trans. Faraday Soc., 1966, 62, 2023.
- ¹⁵ I. W. M. Smith, J. Quant. Spectr. Rad. Transfer, 1968, 8, 1437.
- ¹⁶ J. E. Morgan and H. I. Schiff, J. Chem. Phys., 1963, 38, 1495.
- ¹⁷ F. Kaufman and J. R. Kelso, Symp. Chemiluminescence (Duke University, North Carolina, U.S.A., 1965).
- ¹⁸ A. G. Gaydon, G. H. Kimbell and H. B. Palmer, Proc. Roy. Soc. A, 1964, 279, 313.
- ¹⁹ P. Fowles, M. de Sorgo, A. J. Yarwood, O. P. Strausz and H. E. Gunning, *J. Amer. Chem. Soc.*, 1967, **89**, 1352.
- ²⁰ J.A.N.A.F. Thermochemical Tables (with Addenda 1 and 2) (Nat. Bur. Stand., U.S. Department of Commerce, 1965); Selected Values of Chemical Thermodynamic Properties, (Nat. Bur. Stand., Circ. 500, 1952); ed. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe; E. Neal and L. P. T. Williams, J. Chem. Soc., 1954, 2156; H. Mackle and P. A. G. O'Hare, Trans. Faraday Soc., 1964, 60, 666.
- ²¹ I. W. M. Smith, Disc. Faraday Soc., 1967, 44, 194.
- ²² N. Basco and R. G. W. Norrish, Can. J. Chem., 1960, 38, 1769.
- ²³ J. P. Simons and A. J. Yarwood, Trans. Faraday Soc., 1963, 59, 90.
- ²⁴ F. R. Taylor, A. R. Myerson and P. L. Hanst, J. Chem. Phys., 1957, 26, 1309.
- ²⁵ F. P. Wright, J. Phys. Chem., 1960, 64, 1648.
- ²⁶ R. G. W. Norrish and A. P. Zeelenberg, Proc. Roy. Soc. A, 1957, 240, 293.
- ²⁷ A. V. Jones, J. Chem. Phys., 1950, 18, 1263.
- 28 J. D. Sullivan and P. Warreck, Ber. Bunsenges., 1965, 69, 7.
- ²⁹ W. D. McGrath and J. J. McGarvey, Proc. Roy. Soc. A, 1964, 278, 490.
- ³⁰ R. Meader and E. Miescher, Nature, 1948, 161, 393; R. Meader, Helv. Phys. Acta, 1948, 21, 411.
- ³¹ R. F. Barrow and R. P. du Parcq, *Elemental Sulphur*, ed. C. B. Meyer, (Interscience, New York, 1965).
- ³² B. A. Morrow, *Can. J. Phys.*, 1966, **44**, 2447; W. C. Price, J. P. Tcegan and A. D. Walsh, *Proc. Roy. Soc. A*, 1950, **201**, 600.
- ³³ L. B. Blanchard and P. Le Goff, Can. J. Chem., 1957, 35, 89.
- ³⁴ V. I. Vedeneyev, L. V. Gurvich, V. N. Kondratyev, V. A. Medvedev and Ye L. Frankevich, Bond Energies, Ionisation Potentials and Electron Affinities (Edward Arnold, London, 1966).
- ³⁵ H. D. Smyth and D. W. Meuller, Phys. Rev., 1933, 43, 121.
- ³⁶ Y. Tanaka and H. Ogawa, J. Chem. Phys., 1962, 36, 726.
- ³⁷ F. Alberti, R. A. Ashby and A. E. Douglas, Can. J. Phys., 1968, 46, 337.
- ³⁸ G. Herzberg, Spectra of Diatomic Molecules (Van Nostrand, New York, 1964).