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Reaction of Hydrogen Atoms with Hydrogen Sulphide in the Presence of Molecular Oxygen

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The reaction of H with H_2S in a discharge flow system yields S atoms; these react rapidly with added molecular oxygen,

$$S+O_2 \rightarrow SO+O+6 \text{ kcal/mole}, \tag{1}$$

where $k_1 = (1{\cdot}2 \pm 0{\cdot}3) \times 10^{12}$ cm^3 mole^{-1} sec^{-1} at 298°K. From measurements of the yields of O and SO, excess atomic hydrogen converts 85±15 % of the hydrogen sulphide to atomic sulphur. When excess O_2 is present, SO is removed by OH formed in the reaction sequence,

$$H+O_2+M \rightarrow HO_2+M \tag{7}$$

$$H+HO_2 \rightarrow OH+OH \tag{8b}$$

$$SO+OH \rightarrow SO_2+H. \tag{6}$$

A value of $k_6 = (7 \pm 3) \times 10^{13}$ cm^3 mole^{-1} sec^{-1} at 298°K is obtained by a competitive method.

Free ground state sulphur atoms are produced by the reaction of hydrogen atoms with hydrogen sulphide in a discharge flow system.[1] That work did not prove that S atoms were produced in stoichiometric yield from H_2S, although the mechanism was thought to be

$$H+H_2S = H_2+HS+15 \text{ kcal/mole}$$

$$H+HS = H_2+S+17 \text{ kcal/mole.}$$

This point is established here by examining the effect of molecular oxygen; this converts sulphur atoms to SO by the reaction

$$S+O_2 \rightarrow SO+O+6 \text{ kcal/mole}, \tag{1}$$

which is rapid in flash photolysis systems.[2] Since both SO and O are determined quantitatively in flow systems [3, 4] reaction (1) can be used to measure S atom yields. The decay of SO was more rapid than expected; this is due to reaction with OH radicals formed in a secondary step following the combination reaction $H+O_2+M$.

EXPERIMENTAL

The apparatus has been described [1]; any variations in technique are noted in the text. Up to 1 % of hydrogen atoms were produced by passing 1-5 % hydrogen in an argon carrier through a 100 W 20 MHz electrodeless discharge at total pressures of 1-4 mm Hg.

RESULTS

SPECTROSCOPIC OBSERVATIONS

The hydrogen sulphide flows were similar to those used before [1] (usually less than 5 % of the hydrogen atom flow); molecular oxygen was added upstream from the point of addition of hydrogen sulphide. Under these conditions a pale blue

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chemiluminescence was obtained, the spectrum of which had three features: (i) A continuum extended from about 2400 Å to the long wavelength limit of the plates (about 4800 Å). This continuum was identical with the sulphur dioxide afterglow (generated by reaction of atomic oxygen with carbonyl sulphide [5]) which arises [4] from the chemiluminescent three-body recombination of O and SO. (ii) Very weak bands of the $B^3\Sigma_u^-\rightarrow X^3\Sigma_g^-$ system of S_2 were superimposed on the continuum from 2829 Å to longer wavelenths. The strongest bands were those with $v' = 9,8,7,6$. These were the bands which were most prominent in the S_2 emission spectrum obtained in the absence of oxygen [1] and also presumably arise from the chemiluminescent recombination of sulphur atoms; the removal of sulphur atoms by reaction with oxygen accounts for their much reduced intensity. (iii) Bands of the $B^3\Sigma^-\rightarrow X^3\Sigma^-$ system of SO from levels $v' = 3,2,1$ were observed in the region 2442-2827 Å. The strongest transitions from $v' = 0$ occur [6] at 3064 Å (0,8), 3165 Å (0,9) and 3271 Å (0,10), but these bands could not be positively identified as they were obscured by the O+SO continuum. Level $v' = 3$ lies close to the dissociation limit of ground state SO [7] (which is 123·5 kcal/mole [8]) and this strongly suggests that SO*(*B*) is populated by association of oxygen and sulphur atoms,

$$S+O+M\rightarrow SO^*(B)+M. \qquad (2)$$

The only reaction sufficiently exothermic to excite ground state SO ($v'' = 0$) up to level $v' = 3$ of the *B* state which could occur in the system is

$$SO+O+SO\rightarrow SO_2+SO^*(B) \qquad (3)$$

but this does not occur under conditions similar to ours.[4, 9] This emission therefore shows unequivocally that sulphur atoms are present in our system. It is expected that the SO bands would be more intense than the S_2 bands since the intensity of the latter depends on $[S]^2$ (ref. (1)) while the former must depend on the product [S][O].

The presence of atomic oxygen was confirmed by addition of nitric oxide. The green air afterglow emission was produced and its intensity was proportional to the concentration of nitric oxide added, as expected from the relation,[3]

$$I_a = I_{oa}[O][NO]. \qquad (i)$$

The spectral distribution of the emission was investigated by fitting the photomultiplier with various filters (5480 Å interference filter, and Wratten filters no. 5,45,61,70,72B), and was identical with that of a pure air afterglow in argon (table 1).

TABLE 1

filter	Interference	5	45	61	70	72B
λ(A)	5410-5550	>5000	4500-5100	5000-5600	>6700	5900-6300
I_1	1·00	65·5	8·82	11·6	7·25	1·35
I_a	1·00	70·9	8·80	11·7	7·51	1·34

λ = transmission range of filter, I_1 = normalized photocurrent of the emission from $H+H_2S+O_2+NO$ corrected for HNO and O+SO emission, I_a = normalized photocurrent from pure air afterglow.

MEASUREMENT OF O AND SO CONCENTRATIONS

Oxygen atom concentrations were obtained from the intensity of the air afterglow (using the 5480 Å filter) by relation (i). Concentrations of SO were then determined from the intensity of the sulphur dioxide afterglow, which is given by [9, 4]

$$I_s = I_{os}[O][SO] \qquad (ii)$$

I_s was measured using a 3660 Å interference filter assuming that S_2 emission in this region was negligible. This was certainly true for the conditions used in recording

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the spectrum of the emission. The experiments described here cast no doubt on the validity of this assumption except at very low oxygen flows where S_2 emission caused a sharp increase in the apparent SO concentration calculated from eqn. (ii); this effect was considerably increased by the low oxygen atom concentrations in this region and was simple to detect; concentrations of SO therefore could not be determined at lower O_2 flows.

Fig. 1 and 2 show the results of typical experiments in which various flows of oxygen were added upstream from a constant flow of hydrogen sulphide. Initial hydrogen sulphide concentrations $[H_2S]_0$ between 1 and 3×10^{-11} mole cm^{-3} and reaction times from 0·07 to 0·5 sec were used; concentrations of SO and atomic oxygen comparable to $[H_2S]_0$ were observed. The SO concentration at a fixed observation point downstream decreased as the oxygen flow was raised, and extrapolation to zero oxygen flow yielded an intercept which was usually within 5 % of $[H_2S]_0$; in only one experiment was the discrepancy as high as 10 %.

DECAY OF SO

The reduction in the SO concentration with increasing oxygen flow was small for the shortest reaction time used, but it increased as the reaction time lengthened. The SO decay also increased when the hydrogen atom concentration was raised but this had no effect on the intercept at $[O_2] = 0$. These observations show that the hydrogen sulphide was completely converted to SO in less than 0·07 sec, and the SO was removed by a reaction involving molecular oxygen and atomic hydrogen.

Although the reaction

$$O+SO+M\rightarrow SO_2+M+132 \text{ kcal/mole} \qquad (4)$$

has a high rate constant [4] of $k_4 = 3{\cdot}2\times10^{17}$ cm^6 mole^{-2} sec^{-1}, it accounted for less than 10 % of the observed SO decay. Halstead and Thrush [4] report an upper limit of $k_5<2\times10^8$ cm^3 mole^{-1} sec^{-1} for the reaction

$$SO+O_2\rightarrow SO_2+O+13 \text{ kcal/mole} \qquad (5)$$

and a value of $k_5 = 10^6$ cm^3 mole^{-1} sec^{-1} at 300°K can be estimated from work by Williams.[10] Reaction (5) was therefore negligibly slow under our conditions. The only bimolecular reactions of SO which will be exothermic are those yielding SO_2, and we conclude that the main process removing SO is

$$SO+OH\rightarrow SO_2+H+30 \text{ kcal/mole,} \qquad (6)$$

the OH radicals being formed by the $H+O_2$ reaction, which has the mechanism,[11]

$$\begin{aligned} H+O_2+M&\rightarrow HO_2+M+47 \text{ kcal/mole} && (7)\\ H+HO_2&\rightarrow H_2+O_2+57 \text{ kcal/mole} && (8a)\\ &\rightarrow OH+OH+38 \text{ kcal/mole} && (8b)\\ &\rightarrow H_2O+O+55 \text{ kcal/mole} && (8c)\\ OH+OH&\rightarrow H_2O+O+17 \text{ kcal/mole} && (9)\\ O+OH&\rightarrow O_2+H+17 \text{ kcal/mole} && (10) \end{aligned}$$

under these conditions.

EFFECT OF ADDED NO_2

This deduction was verified by addition of nitrogen dioxide downstream from the hydrogen sulphide inlet jet. Hydroxyl radicals were generated in the rapid reaction

$$H+NO_2\rightarrow OH+NO+29 \text{ kcal/mole} \qquad (11)$$

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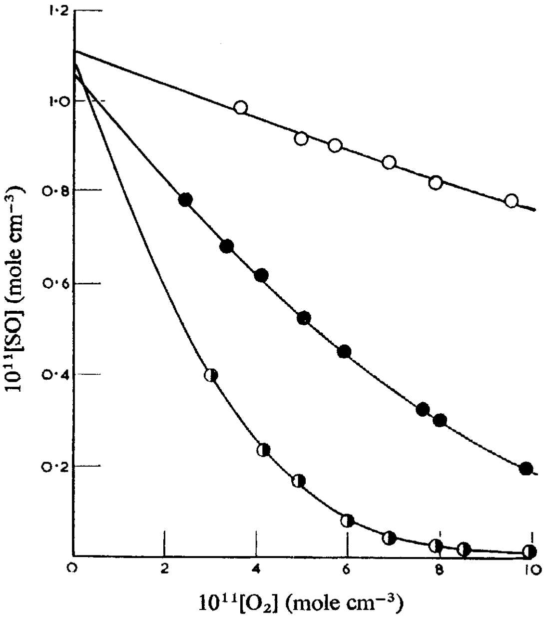

FIG. 1.—Dependence of SO concentration on $[O_2]$. Reaction time (sec): ○, 0·072; ●, 0·207; ◑, 0·482.
$[H_2S]_0 = 1·03 \times 10^{-11}$ mole cm^{-3}.

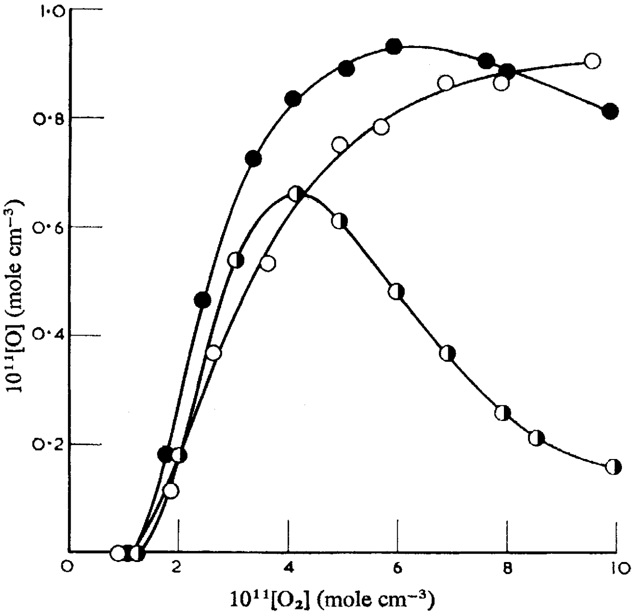

FIG. 2.—Dependence of O atom concentration on $[O_2]$. Reaction time (sec): ○, 0·072; ●, 0·207; ◑, 0·482.
$[H_2S]_0 = 1·03 \times 10^{-11}$ mole cm^{-3}.

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and fig. 3 shows that the concentrations of O and SO further downstream decreased. This was definitely due to reaction with OH and not with NO_2 as under the conditions of the experiments ([O], [SO]$\sim$0·01[H]) less than 0·5 % of the atomic oxygen and the SO could be removed by [12, 13, 9]

$$O+NO_2 \rightarrow O_2+NO+46 \text{ kcal/mole} \tag{12}$$

$$SO+NO_2 \rightarrow SO_2+NO+59 \text{ kcal/mole.} \tag{13}$$

As the nitrogen dioxide was added at a reaction time of 0·14 sec, where the only sulphur species present are SO and SO_2, there could be no complications from reactions of atomic sulphur or S_2.

Since $k_9 = 1\times10^{12}$ cm^3 mole^{-1} sec^{-1},[14, 15] and $k_{10} = 3\times10^{13}$ cm^3 mole^{-1} sec^{-1},[16] few hydroxyl radicals will be removed by reaction (9) provided [OH]$\ll$[O]. The contact time for the nitrogen dioxide (0·07 sec) was sufficient for reaction (10) to go to completion, but it can be seen from fig. 3 that the total concentration of [O]+[SO] removed was less than the concentration of NO_2 added. This appeared to be due to some back diffusion of hydrogen atoms into the nitrogen dioxide jet particularly at the lowest NO_2 flows used. Some of the hydroxyl radicals formed in reaction (11) are then removed by reactions (9) and (10) in the inlet jet. The steady-state concentration of oxygen atoms would then be given by [16]

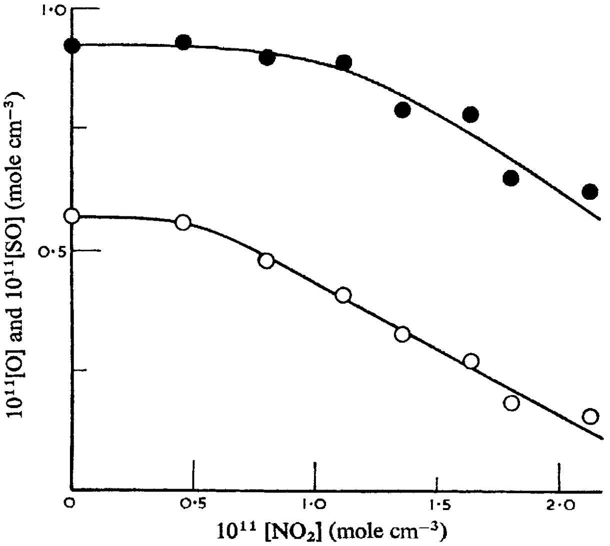

FIG. 3.—Removal of O(●) and of SO (○) by reaction with OH. $[H_2S]_0 = 1·07\times10^{-11}$ mole cm^{-3}; $[O_2] = 5·10\times10^{-11}$ mole cm^{-3}.

$$[O] = k_9/k_{10}[OH] = 0·03\ [OH], \tag{iii}$$

and this extremely small oxygen atom concentration represents the maximum amount which could pass into the flow tube. Diffusion becomes less important as the nitrogen dioxide flow is raised and this explains the plateaus in the curve of fig. 3 at low NO_2 flows.

A value of the ratio k_{10}/k_6 can be determined from the relative decays of the atomic oxygen and the SO on addition of nitrogen dioxide. The rates of reaction of these species are

$$-d[SO]/dt = k_4[O][SO][M]+k_6[SO][OH]$$
$$-d[O]/dt = k_4[O][SO][M]+k_{10}[O][OH]+k_w[O]-\gamma k_7[H][O_2][M]$$

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where $\gamma = k_{8c}/(k_{8a}+k_{8b}+k_{8c})$, and k_w represents surface decay of oxygen atoms. Reaction (4) accounted for less than 5 % of the observed decays and was therefore neglected. Hence, taking the point of nitrogen dioxide addition as zero reaction time, integration of the above expressions yields

$$-\ln\frac{[O]}{[O]_0} = -\frac{k_{10}}{k_6}\ln\frac{[SO]}{[SO]_0} + \int_0^t k_w \mathrm{d}t - \gamma\int_0^t \frac{k_7[H][O_2][M]}{[O]}\mathrm{d}t,$$

and hence under our experimental conditions,

$$\frac{k_{10}}{k_6} = \frac{\mathrm{d}\ln[O]}{\mathrm{d}\ln[SO]} - \gamma\frac{\mathrm{d}}{\mathrm{d}\ln[SO]}\int_0^t \frac{k_7[H][O_2][M]}{[O]}\mathrm{d}t. \qquad \text{(iv)}$$

Fig. 4 shows a plot of $\log_{10}[O]$ against $\log_{10}[SO]$ from which the second term in eqn. (iv) can be obtained. Reaction (7) has a rate constant $k_7 = 1{\cdot}35\times10^{16}$ cm^6 mole^{-2} sec^{-1},[17] and $0<\gamma<0{\cdot}44$ [11]; the third term in eqn. (iv) which contributes 20 % of the final value was estimated assuming that the intergrand did not vary from its value at the observation point. The result obtained was $k_{10}/k_6 = 0{\cdot}40\pm0{\cdot}07$, where the error limits come largely from the considerable uncertainty of γ. The formation of oxygen atoms in the nitrogen dioxide inlet jet due to diffusion of hydrogen atoms could increase this value of k_{10}/k_6 by a maximum of 5 % if all the NO_2 were converted to OH before it entered the flow tube.

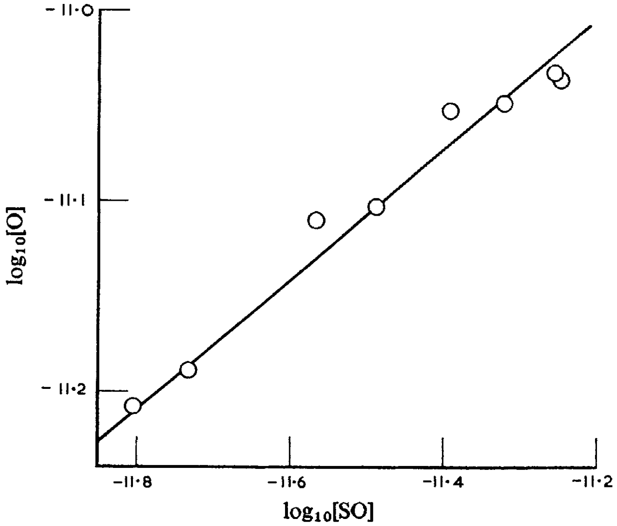

FIG. 4.—Competitive reactions of O and of SO with OH.

SO DECAY IN THE ABSENCE OF NO_2

In the absence of added NO_2, removal of OH radicals by (9) was again negligible compared with (10) due to the presence of appreciable concentrations of atomic oxygen. The steady state concentration of OH is then

$$[OH] = 2\beta k_7[H][O_2][M]/(k_6[SO]+k_{10}[O]),$$

where $\beta = k_{8b}/(k_{8a}+k_{8b}+k_{8c})$. Hence

$$\frac{[H][O_2][M]}{-(\mathrm{d}[SO]/\mathrm{d}t)_6} = \frac{k_{10}}{2\beta k_7 k_6}\frac{[O]}{[SO]} + \frac{1}{2\beta k_7}, \qquad \text{(v)}$$

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where $-(d[SO]/dt)_6$ represents the rate of removal of SO by reaction (6). This was determined graphically by measuring the SO concentration at different reaction times and correcting for SO removal by reaction (4). Plots of the left hand side of eqn. (v) against [O]/[SO] gave good straight lines. The intercepts agreed well with published work,[11, 17] which shows that $3{\cdot}0\times10^{15}<\beta k_7<9{\cdot}0\times10^{15}$ cm^6 mole^{-2} sec^{-1}, and for values of βk_7 in this range the slopes were consistent with the value of $k_{10}/k_6 = 0{\cdot}4$ determined above. That ratio yields $k_6 = (7\pm3)\times10^{13}$ cm^3 mole^{-1} sec^{-1} at 298°K including the uncertainties in k_{10} and the rate constant ratio determined here.

OXYGEN ATOM YIELDS

As the molecular oxygen flow was increased the oxygen atom concentration at a fixed point downstream produced by a constant flow of hydrogen sulphide passed through a maximum (fig. 2). This maximum moved to lower oxygen flows and became much sharper at longer reaction times. The maximum oxygen atom concentration decreased as the reaction time was lengthened but under all the conditions used was between 0·5 and 0·9 of the concentration of hydrogen sulphide added ($[H_2S]_0$). For instance, with a reaction time of 0·07 sec, $[O]_{max}\approx0{\cdot}85[H_2S]_0$ when $[H_2S]_0 = 1\times10^{-11}$ mole cm^{-3}. The decay of the oxygen atoms at molecular oxygen flows greater than that giving maximum [O] increased when the hydrogen atom concentration was raised; this was clearly due to reaction (10), the rate of production of OH by (7) followed by (8*b*) being greater.

According to eqn. (iii), the reaction

$$HS+O_2\rightarrow SO+OH+21\text{ kcal/mole} \qquad (14)$$

followed by (9) and (10) would yield an oxygen atom concentration no greater than $0{\cdot}03\,[H_2S]_0$. The rate of the reaction

$$H+OH\rightarrow H_2+O+2\text{ kcal/mole} \qquad (15)$$

can be calculated from data on the reverse reaction [16] and the equilibrium constant [18]; it was negligibly slow under our conditions. Hence the main source of oxygen atoms is

$$S+O_2\rightarrow SO+O+6\text{ kcal/mole} \qquad (1)$$

as this is the only reaction which can produce the observed oxygen atom concentrations.

At low oxygen flows the concentration of atomic oxygen was very small. Atomic sulphur adsorbs [1] on the surface of the flow tube and several workers [4, 19, 20] have found that SO is formed on reaction of oxygen atoms with solid sulphur. The low oxygen atom concentration can therefore be attributed to removal of the atoms formed in (1) by the reaction

$$O+S_w\rightarrow SO,\ \Delta H^\circ = -58\text{ kcal/mole} \qquad (16)$$

and the rising portion of the oxygen atom curve with increasing oxygen flow (fig. 2) is due to competition between reactions (1) and (16) for the removal of sulphur atoms. Any S_2 formed by the recombination of S atoms or by reaction (17) would be converted to SO by reaction (18):

$$S+HS\rightarrow S_2+H+16\text{ kcal/mole} \qquad (17)$$

$$O+S_2\rightarrow SO+S+22\text{ kcal/mole,} \qquad (18)$$

followed by (1), which together have the stoichiometry

$$O_2+S_2 = 2SO$$

and therefore do not constitute a removal process for oxygen atoms.

The oxygen atom profiles in fig. 2 can be considered as the resultant of two contributions: a formation curve, due to reactions (1), (16) and perhaps (18), which is

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approximately independent of reaction time, and superimposed on this a decay curve due to reaction (10) which becomes more important at longer reaction times. This explains the observation that the maximum oxygen atom concentration is smaller and occurs at lower oxygen flows when the reaction time is increased.

Experiments were performed using a short reaction time (0·05 sec) and a low pressure (0·9 mm Hg) to minimize the formation of OH radicals and oxygen atoms in (8*b*) and (8*c*)respectively. The hydrogen sulphide concentration used was $[H_2S]_0 = 3 \times 10^{-11}$ mole cm^{-3}. Under these conditions the oxygen atom concentration was close to its maximum (*ca.* 70 % yield) for a molecular oxygen concentration of 10×10^{-11} mole cm^{-3}; at this point the total atomic oxygen concentration formed by (7) followed by (8*c*) in the available reaction time was less than $0{\cdot}037[H_2S]_0$ and the hydroxyl radical concentration from (7) followed by (8*b*) was between 0·037 and $0{\cdot}114[H_2S]_0$. The concentration of SO observed at $[O_2] = 10 \times 10^{-11}$ mole cm^{-3} was $0{\cdot}95[H_2S]_0$ which is consistent with complete conversion of the H_2S to SO and removal of 5 % of the SO by reaction with OH. Making allowances for the oxygen atoms present in the discharge products, for those formed in (8*c*) and for the removal of atoms in (10), the concentration of oxygen atoms formed was between 0·66 and 0·70 $[H_2S]_0$. If the reaction mechanism were simply formation of sulphur atoms by (19) and (20) and their removal by (1), then concentrations of O and SO

$$H + H_2S \rightarrow H_2 + HS + 15 \text{ kcal/mole} \qquad (19)$$

$$H + HS \rightarrow H_2 + S + 17 \text{ kcal/mole} \qquad (20)$$

close to $[H_2S]_0$ would be expected. The SO concentration was in good agreement with this, showing that the reaction had proceeded to completion, but the oxygen atom concentration was about 30 % lower.

There are four possible explanations of this discrepancy: (i) the sulphur atoms might remove oxygen atoms on the surface of the flow tube. This implies competition between reactions (16) and (1), and the oxygen atom concentration would be expected to continue rising with increasing oxygen flow, whereas the observed curve appeared to be levelling off at $[O_2] = 10 \times 10^{-11}$ mole cm^{-3}. However, the maximum was not actually attained and since this mechanism requires removal of 85 % of the sulphur atoms by reaction (1) if the O atom yield is 0·7 $[H_2S]_0$, the rise in the oxygen atom curve will be gradual and could have escaped detection.

(ii) The oxygen atoms formed in (1) could be removed by reaction with H_2S or HS:

$$O + H_2S \rightarrow OH + HS + 13 \text{ kcal/mole} \qquad (21)$$

$$O + HS \rightarrow SO + H + 38 \text{ kcal/mole} \qquad (22)$$

The work of Liuti, Dondes and Harteck [21] shows that hydrogen sulphide reacts much more rapidly with hydrogen atoms than with oxygen atoms, and so reaction (21) can be neglected. For H and O atoms to compete for HS radicals would require a lower limit of $k_{22} \approx 12\, k_{20}$ if reaction (1) were assumed to be instantaneous at $[O_2] = 10 \times 10^{-11}$ mole cm^{-3}. Any contribution from the reaction

$$O + HS \rightarrow OH + S + 16 \text{ kcal/mole} \qquad (22a)$$

could not have been important in this experiment since a large proportion of the resulting OH radicals would react with SO in reaction (6) and therefore decrease the observed SO concentration. The concentration of OH radicals formed in (8*b*) during the reaction time was quite low ($<0{\cdot}114[H_2S]_0$). OH radicals can therefore have little influence on the removal of H_2S and so (19) is definitely the dominant reaction removing H_2S.

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(iii) The SH radicals formed in (19) could react with themselves

$$\mathrm{HS+HS \rightarrow H_2S+S+2\ kcal/mole} \quad (23a)$$

$$\mathrm{\rightarrow H_2+S_2+33\ kcal/mole} \quad (23b)$$

Since S_2 can be converted to SO without yielding oxygen atoms, this mechanism requires that 30 % of the HS radicals form S_2. If SH radicals are removed significantly by reaction (23*b*), this process must predominate over reaction (20) because the yield of sulphur atoms in the $H+H_2S$ reaction is unaffected on changing the hydrogen atom concentration by a factor of two.[1] A change of 10 % in the sulphur atom yield would have been detected (i.e., a 20 % change in the intensity of the S_2 emission); hence the lower limit of k_{23b} is $100k_{20}$. The rate constant of reaction (20) has not been measured, but a calculated value [22] of $k_{20} = 2\times10^{11}$ cm^3 mole^{-1} sec^{-1} at 300°K is plausible. This then gives a lower limit of $k_{23b}\approx 2\times10^{13}$ cm^3 mole^{-1} sec^{-1}.

Strausz, Donovan and de Sorgo [23] obtained a value of $k_{23a}+k_{23b} = 1{\cdot}4\times10^{14}$ cm^3 mole^{-1} sec^{-1}, but their data yield no relative rates for reactions (23*a*) and (23*b*). Darwent, Wadlinger and Allard [24] found that this reaction proceeded almost entirely through path (23*a*). The corresponding reaction of OH radicals shows no evidence of the four-centre path corresponding to (23*b*), and present evidence is against the occurrence of rapid four-centre reactions. We therefore consider that (23*b*) cannot be fast enough to play an important role in our system, and note that reactions (19)+(23*a*) and reactions (19)+(20) have the same overall stoichiometry:

$$\mathrm{2H+H_2S = 2H_2+S}$$

(iv) The occurrence of reaction (17) would result in the formation of S_2 rather than S and therefore yield SO without producing oxygen atoms. Reactions (17) and (20) are almost equally exothermic and involve breaking the same bond; it is therefore probable that $k_{17} \sim k_{20}$. If so, (17) is unlikely to compete with (20) for HS since $[\mathrm{H_2S}]_0 = 0{\cdot}04[\mathrm{H}]$, or for this reason to compete to a significant extent with (23*a*) if this is the main second step, that is if $k_{23a} \gg k_{20}$. If competition between reactions (17) and (20) is the explanation of the low yield of atomic oxygen, our results would require a value of $k_{17} = 30k_{20}$.

All the evidence supports the view that atomic sulphur is rapidly produced in nearly stoichiometric yields ($0{\cdot}85\pm0{\cdot}15$) when H_2S reacts with a great excess of hydrogen atoms. The 30 % deficiency of the oxygen atom yield in the presence of O_2 appears to be due to removal of oxygen atoms by reactions (16) or (22) (i.e., cases (i) and (ii) above); our results cannot distinguish these two possibilities.

The occurrence of reaction (1) followed by (4) causes an increase in the intensity of blue and u.v. emission as I_0 for the SO_2 afterglow is greater than for the S_2 emission (by a factor of 2·66 at 3660 Å for an argon carrier at 2·2 mm Hg pressure). This rise in intensity below the point of H_2S addition is more rapid at higher oxygen flows. In determining k_1 by analyzing this intensity rise, allowance must be made for the fact that the SO_2 afterglow only reaches 70 % of its expected intensity. This can be due to either the occurrence of reaction (16) or to the removal of SO and O by OH in reactions (6) and (10); the magnitude of this effect is consistent with the amount of OH produced in the reaction time. If it is assumed that the O and SO concentrations are a fixed percentage of their theoretical values at all reaction times, analysis of the rise gave constant values of $k_1 = (1{\cdot}1\pm0{\cdot}2)\times10^{12}$ cm^3 mole^{-1} sec^{-1}. If this correction is ignored, the value of k_1 decreases with increasing reaction time but extrapolation to $t = 0$, which eliminates the effect of any decay of O or SO, yields $k_1 = (1{\cdot}3\pm0{\cdot}2)\times10^{12}$ cm^3 mole^{-1} sec^{-1}. These two sets of determinations are encompassed by a value of $k_1 = (1{\cdot}2\pm0{\cdot}3)\times10^{12}$ cm^3 mole^{-1} sec^{-1} at 298°K.

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DECAY OF HYDROGEN ATOMS

The hydrogen atom decay in the presence of constant O_2 flows was investigated by adding various flows of hydrogen sulphide and measuring the corresponding hydrogen atom concentrations, $[H]_3$, at a fixed point (reaction time t) downstream. As before,[1] the H_2S is assumed to be rapidly converted to atomic sulphur with the consumption of two hydrogen atoms per H_2S molecule, and the rate constant k_H for the subsequent catalytic decay is defined by

$$-d[H]/dt = k_H[H][H_2S]_0$$

The apparent overall rate constant k'_H for hydrogen atom removal is given by

$$k'_H = -\frac{1}{t}\frac{d\ln([H]_3/[H]_2)}{d[H_2S]_0} = k_H + 2/([H]_0 t),$$

where $[H]_0$ and $[H]_2$ are the hydrogen atom concentrations at the H_2S inlet jet and the observation point respectively in the absence of H_2S. Typical results are shown in fig. 5. As can be seen by comparing fig. 5 and 6, a sudden acceleration of the hydrogen atom decay was observed for H_2S flows greater than that which reduced the oxygen atom concentration to zero; values of k_H and k'_H were obtained from the initial slopes of the hydrogen atom decay plots. Fig. 7 illustrates the dependence of k_H and k'_H on the molecular oxygen concentration, plotted against $1/[O_2]$.

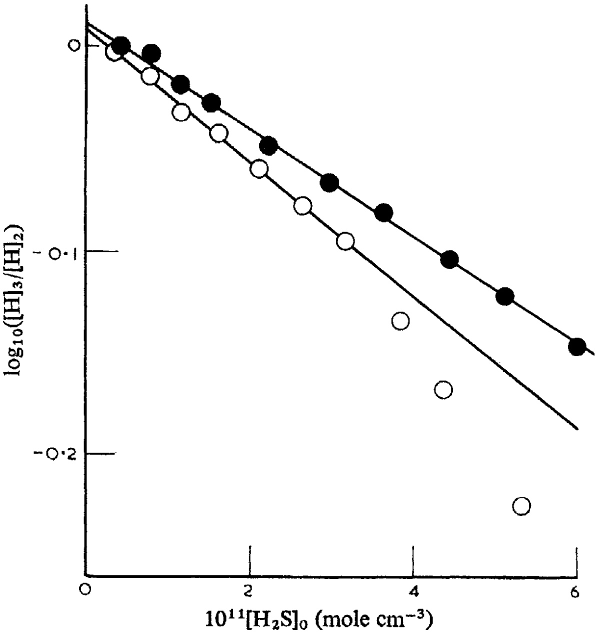

FIG. 5.—First-order plots of hydrogen atom decays in the presence of constant oxygen flows. $t = 0{\cdot}210$ sec; $[M] = 1{\cdot}18\times10^{-7}$ mole cm^{-3}; 10^{11} $[O_2]$ (mole cm^{-3}): ○, 3·17; ●, 9·64

At high $[O_2]$, k'_H approaches zero; i.e., the overall hydrogen atom consumption including reactions (19) and (20) is negligible. The amount of SO produced and the increase in [O] are negligible although reaction (1) is rapid. These unexpected results arise largely because some of the OH radicals produced in (7) followed by (8*b*) react with O and SO formed in (1) by reactions (6) and (10) to give a stoichiometric yield of H atoms rather than yielding $\frac{1}{3}$H by reactions (9) and (10). The remainder of this effect

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is accounted for if OH reacts with H_2S and HS to some extent. For the highest oxygen flows the steady state concentration of OH could reach 0·05[H], and reactions (24) and (25),

$$OH + H_2S \rightarrow H_2O + HS + 30 \text{ kcal/mole} \tag{24}$$

$$OH + HS \rightarrow H_2O + S + 33 \text{ kcal/mole,} \tag{25}$$

might compete effectively with (19) and (20) which are 15 kcal/mole less exothermic and may therefore have lower rate constants. The observed overall stoichiometry

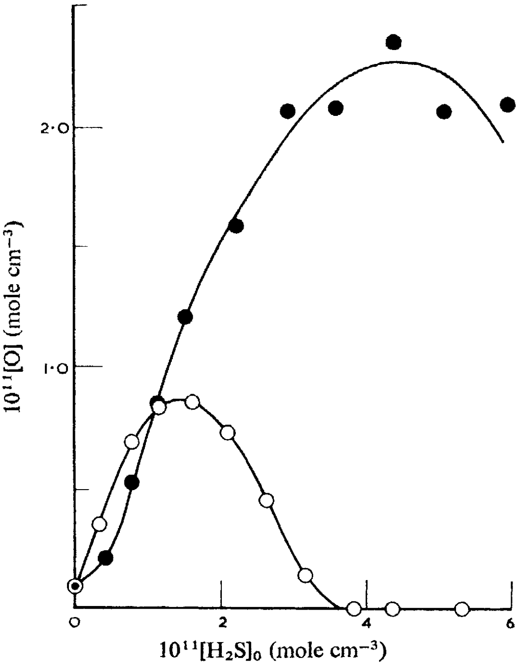

FIG. 6.—Dependence of O atom concentration on $[H_2S]_0$.
t = 0·210 sec; [M] = $1 \cdot 18 \times 10^{-7}$ mole cm^{-3}; $10^{11}[O_2]$ (mole cm^{-3}): ○, 3·17; ●, 9·64.

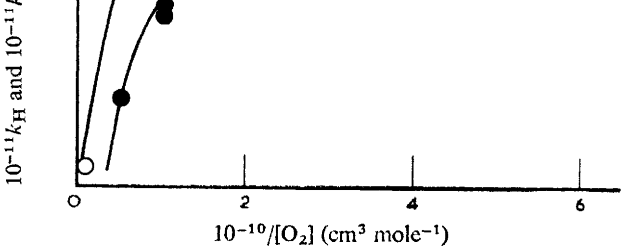

FIG. 7.—Plots of k_H and of k'_H against $1/[O_2]$.
t = 0·210 sec: [M] = $1 \cdot 18 \times 10^{-7}$ mole cm^{-3}. ● = k_H; ○ = k'_H

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provides strong evidence that the destruction of SO yields H atoms, i.e., for reaction (6).

At lower oxygen flows the rate constants k_H and k'_H rose to constant values. Using the value of k_1 determined above, reaction (1) was at least 90 % complete during the reaction time even at the lowest O_2 flow used, and since sulphur atoms can also be removed by reaction (16) all the sulphur atoms were removed before the observation point. Measurements of the SO concentrations confirmed this. If the hydrogen atom decay under these conditions were due to the sulphur atom catalyzed surface removal of hydrogen atoms described previously,[1] the value of k_H would be expected to be approximately inversely proportional to the O_2 concentration since the S atoms are removed more rapidly at higher O_2 flows. However, from fig. 7, k_H was unaffected when the O_2 concentration was changed by a factor of 4, suggesting that another species was responsible for the decay. This species was probably SO. Plots of the SO concentrations against $[H_2S]_0$ were almost linear except for very low H_2S flows where removal of SO in reaction (6) becomes important. In their linear regions the values of $d[SO]/d[H_2S]_0$ changed from 0·7 to 0·95 between the high and low $[O_2]$ ends of the region of fig. 7 where k_H is constant; since this variation of $d[SO]/d[H_2S]_0$ was small, approximately constant values of k_H would be expected here if SO were the catalytic species.

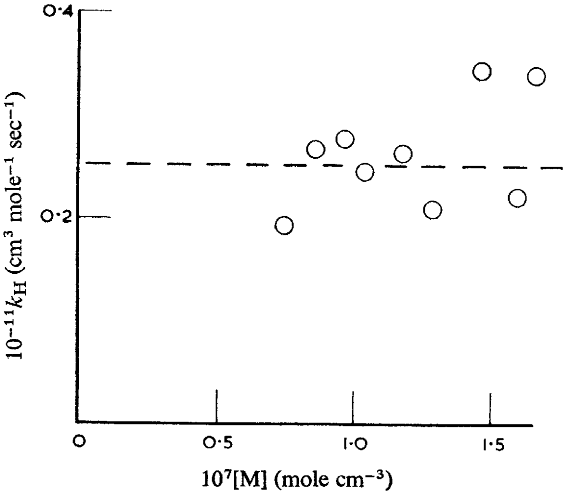

FIG. 8.—Pressure dependence of k_H. The broken line represents the limiting value of k_H in fig. 7.
$t = 0{\cdot}210$ sec; $[O_2] = 2{\cdot}52\times10^{-11}$ mole cm^{-3}.

The second-order reactions

$$H+SO \rightarrow HS+O-38 \text{ kcal/mole} \quad (26a)$$
$$\rightarrow OH+S-22 \text{ kcal/mole} \quad (26b)$$

are strongly endothermic, and therefore any homogeneous catalysis would be third order

$$H+SO+M \rightarrow HSO+M \quad (27)$$
$$H+HSO \rightarrow H_2+SO \quad (28)$$

However, the value of k_{27} needed would be $>10^{17}$ cm^6 mole^{-2} sec^{-1}, and there was no clear evidence that k_H had a significant pressure dependence (see fig. 8). It was

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therefore concluded that the reaction is heterogeneous, the scatter being associated with variable surface conditions.

The H_2S flow at which the oxygen atom concentration decreases to zero presumably corresponds to complete removal of O_2 and O in reactions (1) and (16). At higher flows the additional sulphur atoms will not be removed and these will cause the accelerated hydrogen atom decay observed (fig. 5 and 6).

DISCUSSION

It is unexpected that OH reacts more rapidly with SO than with O($k_6 = 2{\cdot}5k_{10}$), but a similar effect is observed with NO_2, where $k_{13} = 1{\cdot}5k_{12}$(ref. (9)). In both cases the effect of the 12 kcal/mole greater exothermicity of the reactions of SO must outweigh the greater decrease of entropy on activation due to the loss of rotation of SO. In terms of the transition state theory, k_6 and k_{10} are so large that the difference between them cannot be accounted for in terms of a difference in activation energies, but in terms of a difference of $\Delta\varepsilon_0^{\ddagger}$ values which must be negative to give a sufficient density of energy levels in the transition state.

The value of $k_1 = (1{\cdot}2 \pm 0{\cdot}3) \times 10^{12}$ cm^3 mole^{-1} sec^{-1} is reasonable when compared with the closely related isotope exchange reaction

$$O + O_2 \rightarrow O_2 + O \tag{29}$$

for which rate constants of $0{\cdot}6 \times 10^{12}$ and $1{\cdot}0 \times 10^{12}$ cm^3 mole^{-1} sec^{-1} have been reported [25, 26] also at room temperature. Our value of k_1 is also consistent with Callear's observation [2] in the flash photolysis of CS_2 that 5 mm Hg of O_2 is sufficient to decrease the concentration of sulphur atoms below the limit of detectability in 10μsec.

The present work shows clearly that the addition of molecular oxygen provides a useful tool in investigating the reactions of sulphur atoms in the gas phase, and that the reaction of excess atomic hydrogen with hydrogen sulphide provides a useful stoichiometric source of sulphur atoms. However, the complexity of the reactions observed here, and possible presence of species such as S_2 in other systems, stress the need to measure the concentrations of as many active species as possible in such reactions.

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