

## KINETIC STUDY OF GROUND STATE ANTIMONY ATOMS Sb( $5^4S_{3/2}$ ) BY ATOMIC ABSORPTION SPECTROSCOPY

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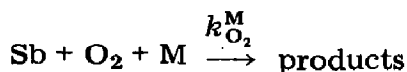
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### Summary

A study of the collisional behaviour of ground state antimony atoms Sb( $5p^3(4S_{3/2})$ ) in the presence of various gases is presented. The atoms were generated by the low energy pulsed irradiation of SbMe<sub>3</sub> and monitored photoelectrically by time-resolved atomic absorption spectroscopy in the "single shot" mode. Attenuation of the resonance transition employed ( $5p^26s(4P_{1/2}) \leftarrow 5p^3(4S_{3/2}^0)$ ,  $\lambda = 231.1$  nm) was investigated in some detail, including measurement of the departure from the Beer-Lambert law using the standard modified expression  $I_{tr} = I_0 \exp \{-\epsilon(c)^\gamma\}$  for which it was found that  $\gamma(\lambda = 231.1 \text{ nm}) = 0.34 \pm 0.03$ . Third order kinetics were found for the removal of Sb( $5^4S_{3/2}$ ) by C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> in the presence of the gases He, N<sub>2</sub> and SF<sub>6</sub> for which the following absolute rate constants are reported. For the reaction Sb + C<sub>2</sub>H<sub>4</sub> + M, the values of  $k_{C_2H_4}^M$  (cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>, at room temperature) obtained were  $(1.0 \pm 0.1) \times 10^{-32}$  for M = He,  $(1.1 \pm 0.1) \times 10^{-32}$  for M = N<sub>2</sub> and  $(1.15 \pm 0.2) \times 10^{-32}$  for M = SF<sub>6</sub>. For the reaction Sb + C<sub>2</sub>H<sub>2</sub> + M, the values of  $k_{C_2H_2}^M$  (cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>, at room temperature) obtained were  $(9.4 \pm 0.1) \times 10^{-33}$  for M = He,  $(1.0 \pm 0.1) \times 10^{-32}$  for M = N<sub>2</sub> and  $(1.2 \pm 0.14) \times 10^{-32}$  for M = SF<sub>6</sub>.

Removal in the presence of NO, for which atom transfer would be endothermic, nevertheless exhibited second order kinetics for which we report  $k_{NO}(\text{He, N}_2, \text{SF}_6) = (1.8 \pm 0.2) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (at room temperature). Reactions in the presence of the gases Cl<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>O and SbMe<sub>3</sub> were also studied, leading to the following rate data:  $k_{SbMe_3} = 2.3 \pm 0.2 \times 10^{-11}$  and  $k_{N_2O} < 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (at room temperature). Third order kinetics were observed for removal in the presence of O<sub>2</sub>. We report the following data for the overall process:



The values of  $k_{\text{O}_2}^{\text{M}}$  (cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>, at 300K) were  $(2.2 \pm 0.2) \times 10^{-31}$  for M = He,  $(3.2 \pm 0.3) \times 10^{-31}$  for M = N<sub>2</sub> and  $(3.6 \pm 0.4) \times 10^{-31}$  for M = SF<sub>6</sub>.

The rate data are compared with the analogous data obtained hitherto for Bi( $6^4S_{3/2}$ ) and, where appropriate, rates are considered within the context

of symmetry arguments employing ( $J, \Omega$ ) coupling to describe the nature of the potential surfaces involved. We believe this work to constitute the first direct and detailed investigation of the collisional behaviour of the ground state antimony atom.

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## Introduction

We have recently stressed [1] that direct kinetic studies of Group V atoms in various states arising from the overall  $np^3$  ground state electronic configuration, which have been concerned principally with the relationship between reactivity and electronic structure [2 - 4], have hitherto concentrated experimentally on the optically metastable  $np^3(^2D_J)$  and  $np^3(^2P_J)$  states. Until very recently studies on Group V ground state atoms were essentially confined to nitrogen atoms  $N(2^4S_{3/2})$  for which powerful spectroscopic marker techniques have been developed [5 - 8] and which have also been studied directly in flow systems by resonance absorption spectroscopy in the vacuum ultraviolet [9, 10]. Husain and Norris [11] have now reported detailed kinetic studies of ground state phosphorus atoms  $P(3^4S_{3/2})$  generated by flash photolysis and monitored photoelectrically in absorption by attenuation of atomic resonance radiation in the vacuum ultraviolet. The present authors have presented a kinetic investigation of ground state bismuth atoms [1]  $Bi(6^4S_{3/2})$ , monitoring this species using resonance absorption spectroscopy following flash photolysis. In this paper, we present a study of the collisional behaviour of ground state antimony atoms  $Sb(5^4S_{3/2})$  by a technique similar to that described for  $Bi(6^4S_{3/2})$ .

One may emphasise that the systematic study of heavy atom collisions is emerging from obscurity for various reasons, three of which merit consideration. Firstly, the collisional behaviour of atomic states involved in the operation of visible atomic transition lasers is of considerable topical interest. This is a large area of research. One may mention the copper atom lasers  $Cu\ 3d^94s^2$  ( $^2P_{3/2}^0 \rightarrow ^2D_{3/2}$  and  $^2P_{3/2}^0 \rightarrow ^2D_{5/2}$ ) as recent examples [12, 13]. Secondly, there has been considerable effort in recent years in the study of heavy atom-molecule collisions which, it is hoped, will lead eventually to molecular electronic transition lasers derived from the chemical products of such reactions [14 - 23]. Thirdly, there is now a better understanding of the relationship between atomic reactivity and electronic structure; symmetry arguments on the nature of the potential surfaces based on the weak spin orbit coupling approximation [24] are appropriate for light atom-molecule collisions, and ( $J, \Omega$ ) coupling for heavy atom-molecule collisions [4, 25].

## Experimental

$Sb(5^4S_{3/2})$  was generated by the pulsed irradiation ( $E = 360\text{ J}$ ) of low pressures of  $SbMe_3$  (typically  $p_{SbMe_3}$  is about  $0.27\text{ N m}^{-2}$ ), generally in the

presence of excess helium buffer gas ( $p_{\text{He}}$  about  $5.3 \text{ kN m}^{-2}$ ) to ensure that there was no significant temperature rise above ambient conditions on photolysis. The exceptions to this occurred in those experiments involving high pressures of other gases chemically inert in this context (*e.g.*  $\text{N}_2$  and  $\text{SF}_6$ ) whose presence had a similar effect on the total reactant heat capacity. The absorption of the resulting Sb atoms was then monitored photoelectrically by attenuation of atomic resonance radiation in the "single shot" mode, as described previously [1].

Unlike the previous studies on  $\text{Bi}(6^4\text{S}_{3/2})$  [1] and those on the metastable states  $\text{Bi}(6^2\text{D}_{3/2, 5/2})$  [26] and  $\text{Sb}(5^2\text{D}_{3/2, 5/2})$  [27], the resonance source in this work was not a flow lamp but a sealed microwave-powered source. However, by contrast with previous line attenuation studies on, for example,  $\text{As}(4^2\text{D}_J, 4^2\text{P}_J)$  [28, 29] which did utilise a sealed source, the present system employed neither a C-111 cavity (E.M.I.) nor a commercial electrodeless discharge tube (E.M.I.). The microwave cavity was of the type described by Fehsenfeld *et al.* [30] which has been employed by Davis and Braun [31] for the construction of flow line emission sources (especially for the vacuum ultraviolet) and used by us for time-resolved studies in that spectral region [32 - 34]. The sealed quartz discharge tube for this study was prepared in the laboratory and the procedure for its construction is critical if a high light output is to be achieved. The basis of the design was similar to that employed in commercial devices (*e.g.* E.M.I. [28, 29]) with particular care being taken to ensure that (1) the  $\text{SbI}_3$  and Sb filling powders were completely dry; (2) the Sb and  $\text{SbI}_3$  were sublimed under vacuum into the discharge region of the tube; and (3) the pressure of the argon filling (about 1 Torr =  $133 \text{ N m}^{-2}$ ) was carefully controlled until the lamp gave a maximum emission from a microwave source operating on the vacuum system used for the lamp construction. This yielded a light source which we believe to be considerably superior in both intensity and stability to previous commercial devices. The intensity of the resonance source is especially important in the present type of time-resolved experiment where the signal-to-noise ratio is critical and where it is desirable to use relatively small slit widths in order to minimise the effect of scattered light from the photolysis pulse. Using this resonance source, the transitions shown in Table 1 were employed in this investigation.

TABLE 1

| Transition  | $\lambda(\text{nm})$ [35] | $10^{-8}gA (\text{s}^{-1})$ [35] |
|---|---------------------------|----------------------------------|
| $6s(4^1\text{P}_{1/2}) \rightarrow 5p^3(4^1\text{S}_{3/2}^0)$ | 231.1                     | 1.5                              |
| $6s(2^1\text{P}_{1/2}) \rightarrow 5p^3(2^1\text{D}_{3/2}^0)$ | 259.8                     | 64                               |
| $6s(2^1\text{P}_{3/2}) \rightarrow 5p^3(2^1\text{D}_{5/2}^0)$ | 252.9                     | 56                               |

The transient light intensity at the appropriate resonance wavelength, representing temporal light absorption by the atomic state generated by the

photolytic pulse, was detected by means of a photomultiplier tube (E.M.I. 9783B) mounted on the exit slit of a Seya-Namioka grating monochromator [28]. The signals were subsequently amplified by means of a current-to-voltage converter employing a fast settling operational amplifier [36] to avoid signal distortion. The pulses were then digitised and stored in a transient recorder (Datalab, DL 905) and the 1024 word memory divided by means of two time bases into two groups as described previously [1], 824 points for recording the transient signal and the remaining 200 points for recording in one second the  $I_0$  value (the unattenuated signal) for each decay. The contents of the recorder were subsequently punched onto paper tape (Data-dynamics punch model 1133) in ASCII code for analysis in the University's computer (I.B.M. 370).

### Materials

SbMe<sub>3</sub>, He, Kr, N<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>O, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and SF<sub>6</sub> were prepared essentially as described previously [1, 26, 27]. The preparation of Cl<sub>2</sub> has also been described [37].

### Results and discussion

Sb(<sup>5</sup>S<sub>3/2</sub>) is readily generated by the low energy irradiation ( $E = 360$  J) of SbMe<sub>3</sub> in a standard quartz reactor and vessel flash photolysis assembly ( $\lambda > 200$  nm). This is seen from the computerised output of the digitised form of the transmitted light intensity of the ground state resonance transition at  $\lambda = 231.1$  nm following photolysis (Fig. 1) and which shows the decay of resonance absorption with time. By contrast, neither Sb(<sup>5</sup>D<sub>3/2</sub>) nor Sb(<sup>5</sup>D<sub>5/2</sub>) were detected in these experiments via the resonance transitions at  $\lambda = 252.9$  and  $259.8$  nm, respectively. This is to be expected since the low-lying <sup>2</sup>D states could previously only be monitored with considerable difficulty using a coaxial lamp and vessel assembly with a common wall of high purity quartz (Spectrosil,  $\lambda > 165$  nm) and with a higher energy discharge ( $E = 1125$  J) through N<sub>2</sub>, which was designed to shift to lower wavelengths the spectral output of the flash lamp [27]. Hence we can neglect any effects of cascading into the <sup>4</sup>S ground state from the optically metastable <sup>2</sup>D<sub>*j*</sub> levels and any accompanying effects on the kinetics.

In our work on Bi(<sup>6</sup>S<sub>3/2</sub>) [1] we employed the standard Beer-Lambert law

$$I_{tr} = I_0 \exp(-\epsilon cl) \quad (1)$$

(the symbols have their usual significance) for the  $\lambda = 306.77$  nm resonance transition (Bi(<sup>7</sup>P<sub>1/2</sub>) ← Bi(<sup>6</sup>S<sub>3/2</sub>)). We did not attempt to measure any deviations from this law for our experimental conditions since this would have involved a higher accuracy in the intercepts of the first order kinetic plots than was obtained in the experiments. In this work the intercepts in the first order kinetic plots, namely  $\ln \{I_0/I_{tr}\}$  ( $\lambda = 231.1$  nm) (which is a

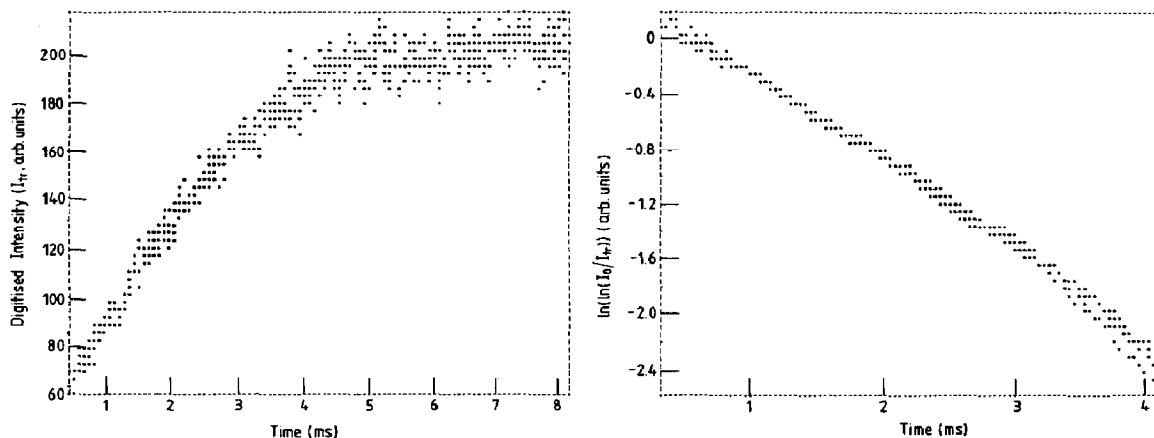


Fig. 1. Digitised time variation of the transmitted light intensity at  $\lambda = 231.1$  nm ( $\text{Sb}(6^4\text{P}_{1/2}) \leftarrow \text{Sb}(5^4\text{S}_{3/2}^0)$ ) indicating the decay of resonance absorption by ground state antimony atoms.  $p_{\text{SbMe}_3} = 0.27 \text{ N m}^{-2}$ ,  $p_{\text{total with He}} = 5.3 \text{ kN m}^{-2}$ ;  $E = 360 \text{ J}$ .

Fig. 2. Typical pseudo first order plot for the decay of  $\text{Sb}(5^4\text{S}_{3/2})$  obtained by monitoring the absorption of light at  $\lambda = 321.1$  nm ( $\text{Sb}(6^4\text{P}_{1/2}) \rightarrow \text{Sb}(5^4\text{S}_{3/2}^0)$ ).  $p_{\text{SbMe}_3} = 0.27 \text{ N m}^{-2}$ ,  $p_{\text{total with He}} = 5.3 \text{ kN m}^{-2}$ ;  $E = 360 \text{ J}$ .

linear function of  $\ln [\text{Sb}(5^4\text{S}_{3/2})]$  versus time, permitted investigation of the modified Beer–Lambert law in one of its forms [1, 38]:

$$I_{\text{tr}} = I_0 \exp \{-\epsilon(ct)^\gamma\} \quad (2)$$

$$I_{\text{tr}} = I_0 \exp \{-\epsilon c l^\gamma\} \quad (3)$$

Figure 2 shows the computerised output of the first order plot for the decay of  $\text{Sb}(5^4\text{S}_{3/2})$  taken directly from the data of Fig. 1 and using the numerical data smoothing procedure of Savitsky and Golay [39]. Making the usual assumption that, for a given pulse energy,  $[\text{Sb}(5^4\text{S}_{3/2})] (t = 0) \propto p_{\text{SbMe}_3}$ , then, on the basis of eqns. (2) and (3), the intercepts of the first order plots  $\ln \{\ln (I_0/I_{\text{tr}})\} (t = 0)$  ( $\lambda = 231.1$  nm) versus  $\ln p_{\text{SbMe}_3}$  (initial) (the so-called Beer–Lambert plot) yield a straight line of slope  $\gamma$  if  $\gamma$  can be taken as constant over a suitable region of atomic particle density. The result is shown in Fig. 3 for the present investigation, yielding  $\gamma = 0.34 \pm 0.03$ .

We may emphasise that eqns. (2) and (3), at least in logarithmic form, have a physical basis provided that for eqn. (2)  $\epsilon$  is not identified with the standard extinction coefficient but is a floating variable of dimensions  $(cl)^{-\gamma}$ . Phillips [40] has calculated “curves of growth” [41] for the  $\lambda = 115.2$  nm resonance transition ( $\text{O}(3^1\text{D}_2^0) \leftarrow \text{O}(2^1\text{D}_2)$ ) using a “three layer” model [42] and found that there are ranges of  $[\text{O}(2^1\text{D}_2)]$  in the reactant path in which  $\gamma$  can be taken to be effectively constant over a sensible range and, in his calculations,  $\gamma$  is about 0.5 once the region of Beer–Lambert behaviour ( $\gamma = 1$ ) has effectively been passed. Husain and Norris [43] confirmed these findings when the small degree of Lorentz broadening in the spectroscopic “two layer” source was also included.

A further aspect of importance here is the nuclear spin ( $I$ ) of the two isotopes of antimony,  $^{121}\text{Sb}$  ( $I = 5/2$ ) and  $^{123}\text{Sb}$  ( $I = 7/2$ ) [44]. Using the

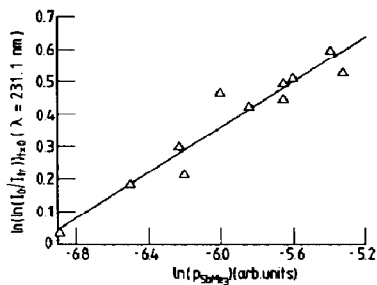


Fig. 3. A Beer-Lambert plot for the  $\lambda = 231.1$  nm transition  $\text{Sb}(6s(4P_{1/2}) \leftarrow 5p^3(4S_{1/4}))$ ;  $P_{\text{total}}$  with He =  $5.3 \text{ kNm}^{-2}$ ;  $E = 360$  J.

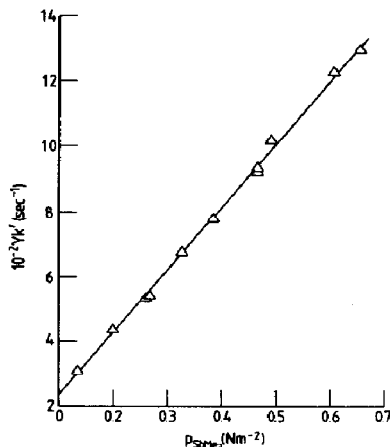


Fig. 4. Pseudo first order rate coefficients ( $\gamma k'$ ) for the decay of  $\text{Sb}(5^4S_{3/2})$  in the presence of  $\text{SbMe}_3$ .  $P_{\text{total}}$  with He =  $5.3 \text{ kNm}^{-2}$ ;  $E = 360$  J;  $T = 293$  K.

simple vector model for nuclear hyperfine interaction, which is adequate for our present purposes, and the standard selection rules  $\Delta F = 0, \pm 1$  [45] it can be seen that the  $\lambda = 231.1$  nm resonance line will in fact comprise 12 lines. Tellinghuisen and Clyne [46] have described a line summation procedure for curve of growth calculations in order to calculate oscillator strengths for halogen atom transitions where nuclear hyperfine splitting is large. Husain and Norris [11] have presented a "three layer model" curve of growth calculation for the transition  $\text{P}(4s(4P_{5/2}) \leftarrow 3p^3(4S_{3/2}))$  ( $\lambda = 177.50$  nm) which includes the effect of nuclear hyperfine interaction ( $I = 1/2$ ). The general shape of the curve is similar to that described above for the  $\lambda = 115.2$  nm transition for  $\text{O}(2^1D_2)$  and yields a region of concentration where  $\gamma$  can be taken to be effectively constant and less than unity. In the case of the Sb atom a curve of growth summation over the 12 lines (including interactions arising from the nuclear quadrupoles and magnetic dipoles) and matching with the data of Fig. 3 would be an undertaking in itself. The object of the foregoing discussion is to demonstrate that the value of  $\gamma$  observed in these experiments is sensible, that it clearly has a complex physical basis and that it can be used in the kinetic analysis arising from the line attenuation measurements.

An example of a kinetic analysis on line attenuation by  $\text{Sb}(5^4S_{3/2})$  leading to absolute rate data arises from the slopes of the first order plots (e.g. Fig. 2) employed to generate the "Beer-Lambert" plot. The slopes of such plots, which are given by  $-\gamma k'$  (eqns. (2) and (3)) are assumed to follow the form

$$k' = K + k_R[R] \quad (4)$$

where  $k'$  is the overall first order decay coefficient,  $K$  a constant in a series of

kinetic experiments in which only the concentration of the reactant R is varied, and  $k_R$  the absolute second order rate constant for the reaction. Figure 4 shows the decay of  $\text{Sb}(5^4\text{S}_{3/2})$  in the presence of varying pressures of the parent molecule  $\text{SbMe}_3$  in the form of eqn. (4) ( $\gamma k'$ ). The slope of this plot, with the above value of  $\gamma$ , yields  $k_{\text{SbMe}_3} = (2.3 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (room temperature). This rate, representing a collisional removal probability of about 0.1, indicates that suitable concentrations of  $\text{Sb}(5^4\text{S}_{3/2})$  should be generated in pulsed experiments of this type which should later permit time-resolved resonance fluorescence investigation of the collisional behaviour of this atomic state at elevated temperatures. In the present experiments particle densities of  $\text{Sb}(5^4\text{S}_{3/2})$  must be employed which do not give rise to resonance line saturation.

### $\text{Sb} + \text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_2$

Figure 5 shows the decay of  $\text{Sb}(5^4\text{S}_{3/2})$  in the presence of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  in the form of eqn. (4). As would be expected by comparison with the analogous data for  $\text{Bi}(6^4\text{S}_{3/2})$  [1], the decay of  $\text{Sb}(5^4\text{S}_{3/2})$  in the presence of these unsaturated molecules exhibited clear third order kinetics. Figures 6 and 7 show the dependence of the first order removal coefficient for antimony atoms

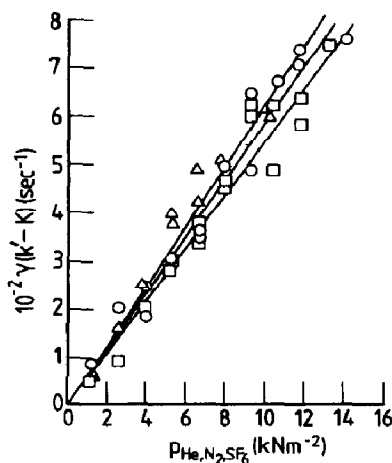
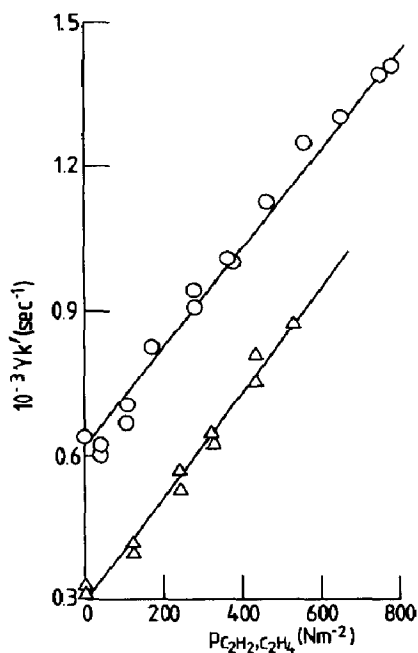


Fig. 5. Pseudo first order rate coefficients  $\gamma k'$  for the decay of  $\text{Sb}(5^4\text{S}_{3/2})$  in the presence of acetylene and ethylene (third body He).  $p_{\text{SbMe}_3}$  ( $\text{Nm}^{-2}$ ): 0.27 (for  $\text{C}_2\text{H}_2$ ), 0.19 (for  $\text{C}_2\text{H}_4$ );  $p_{\text{total}}$  with He =  $5.3 \text{ kNm}^{-2}$ ;  $E = 360 \text{ J}$ ;  $\circ \text{C}_2\text{H}_2$ ;  $\triangle \text{C}_2\text{H}_4$ .

Fig. 6. Pseudo first order rate coefficients  $\gamma(k' - K)$  for the decay of  $\text{Sb}(5^4\text{S}_{3/2})$  in the presence of ethylene with different third bodies (M).  $p_{\text{SbMe}_3} = 0.27 \text{ N m}^{-2}$ ,  $p_{\text{C}_2\text{H}_4} = 266 \text{ N m}^{-2}$ ;  $E = 360 \text{ J}$ ;  $T = 293 \text{ K}$ ;  $\square \text{He}$ ;  $\circ \text{N}_2$ ;  $\triangle \text{SF}_6$ .

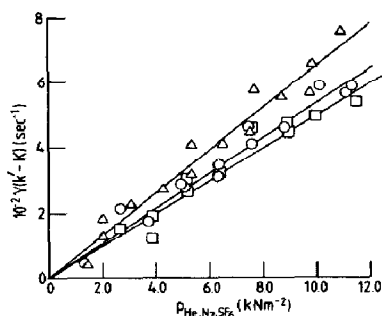


Fig. 7. Pseudo first order rate coefficients  $\gamma(k' - K)$  for the decay of  $\text{Sb}(5^4\text{S}_{3/2})$  in the presence of acetylene with different third bodies (M).  $p_{\text{SbMe}_3} = 0.27 \text{ N m}^{-2}$ ,  $p_{\text{C}_2\text{H}_2} = 266 \text{ N m}^{-2}$ ;  $E = 360 \text{ J}$ ;  $\square$  He;  $\circ$   $\text{N}_2$ ;  $\triangle$   $\text{SF}_6$ .

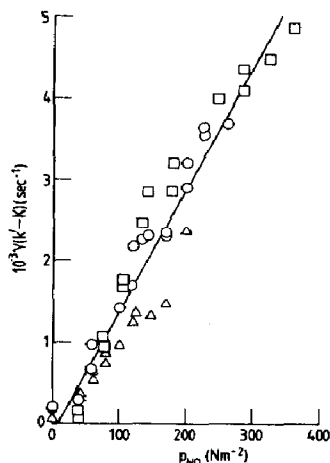
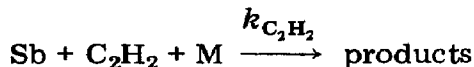
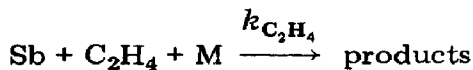


Fig. 8. Pseudo first order rate coefficients  $\gamma(k' - K)$  for the decay of  $\text{Sb}(5^4\text{S}_{3/2})$  in the presence of nitric oxide and He,  $\text{N}_2$  and  $\text{SF}_6$ .  $p_{\text{SbMe}_3} = 0.27 \text{ N m}^{-2}$ ,  $p_{\text{He}, \text{N}_2, \text{SF}_6} = 5.3 \text{ kN m}^{-2}$ ;  $E = 360 \text{ J}$ ;  $\square$  He;  $\circ$   $\text{N}_2$ ;  $\triangle$   $\text{SF}_6$ .

with  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  on the pressure of added He,  $\text{N}_2$  and  $\text{SF}_6$ . These plots yield the overall third order rate constants for the removal processes (Table 2)



which can be compared with the analogous data for  $\text{Bi}(6^4\text{S}_{3/2})$  [1].

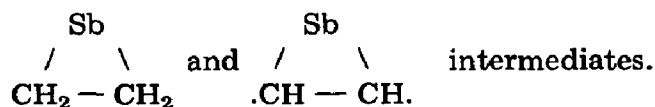
TABLE 2

Third order rate constants ( $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ , at room temperature) for the collisional removal of  $\text{Sb}(5^4\text{S}_{3/2})$  and  $\text{Bi}(6^4\text{S}_{3/2})$  by  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  in the presence of He,  $\text{N}_2$  and  $\text{SF}_6$

| M             | $\text{Sb}(5^4\text{S}_{3/2})$ |                                | $\text{Bi}(6^4\text{S}_{3/2})$ [1] |                               |
|---------------|--------------------------------|--------------------------------|------------------------------------|-------------------------------|
|               | $k_{\text{C}_2\text{H}_4}$     | $k_{\text{C}_2\text{H}_2}$     | $k_{\text{C}_2\text{H}_4}$         | $k_{\text{C}_2\text{H}_2}$    |
| He            | $1.0 \pm 0.1 \times 10^{-32}$  | $9.4 \pm 0.1 \times 10^{-33}$  | $8.3 \pm 1.4 \times 10^{-34}$      | $1.1 \pm 0.1 \times 10^{-33}$ |
| $\text{N}_2$  | $1.1 \pm 0.1 \times 10^{-32}$  | $1.0 \pm 0.1 \times 10^{-32}$  | $2.2 \pm 0.2 \times 10^{-33}$      | $7.4 \pm 0.2 \times 10^{-33}$ |
| $\text{SF}_6$ | $1.15 \pm 0.2 \times 10^{-32}$ | $1.2 \pm 0.14 \times 10^{-32}$ | $4.7 \pm 0.3 \times 10^{-33}$      | $6.5 \pm 0.4 \times 10^{-33}$ |

The third order kinetics for the removal of  $\text{Sb}(5^4\text{S}_{3/2})$  presumably indicate, as with  $\text{Bi}(6^4\text{S}_{3/2})$  [1], initial collisional stabilisation of the





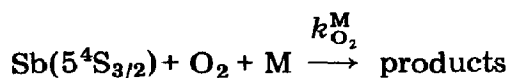
The data for Sb clearly exhibited third order kinetics with  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  (Figs. 6 and 7) although the variation in the third order rate constants was smaller than that observed for the corresponding sets of data for Bi (Table 2). The rates for the two atoms are clearly of comparable magnitude with both unsaturated molecules, indicating intermediate lifetimes of the order of  $10^{-12}$  -  $10^{-13}$  s. For  $\text{Bi} + \text{C}_2\text{H}_4 + \text{He}$   $k_{\text{C}_2\text{H}_4}^{\text{He}} = (1.6 \pm 0.1) \times 10^{-32} \exp \{(-4.0 \pm 0.4 \text{ kJ mol}^{-1}) / RT\} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  [1] but we were unable to detect a significant activation energy for the analogous removal process for Sb.

### *Sb + NO*

Like Bi [1],  $\text{Sb}(5^4\text{S}_{3/2})$  exhibited second order kinetics with NO. The pressure of helium was varied from  $1.33 \text{ kN m}^{-2}$  to  $13.3 \text{ kN m}^{-2}$  with no discernible difference in the decay rate of the atom. Figure 8 shows the data ( $\gamma k'$ ) for the removal of the antimony atoms with NO in the presence of He,  $\text{N}_2$  and  $\text{SF}_6$ . No significant differences could be detected for the three buffer gases although the plot in Fig. 8 shows greater scatter than the analogous plot for Bi [1]. The second order rate constant derived from these data for Sb is given by  $k_{\text{Sb} + \text{NO}}(\text{He}, \text{N}_2, \text{SF}_6) = (1.8 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (room temperature) which is close to the analogous result for Bi ( $k_{\text{Bi} + \text{NO}}(\text{He}, \text{N}_2, \text{SF}_6) = 5.6 \pm 0.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1}$  at room temperature [1]) and indicates a strong intermediate in both cases. A reaction to yield  $\text{SbO} + \text{N}$  or  $\text{SbN} + \text{O}$  would be highly endothermic ( $\Delta H = +2.5$  and  $+3.4 \text{ eV}$ , respectively [47]).

### *Sb + O<sub>2</sub> + M*

Previous measurements on the collisional removal of  $\text{Bi}(6^4\text{S}_{3/2})$  by  $\text{O}_2$  yielded kinetic decays exhibiting a complex dependence on  $[\text{O}_2]$  and on  $[\text{He}]$ . By contrast, the kinetics for the removal of  $\text{Sb}(5^4\text{S}_{3/2})$  by  $\text{O}_2$  were found to be straightforward. Firstly,  $\text{Sb}(5^4\text{S}_{3/2})$  gave rise to good first order decays in the presence of  $\text{O}_2$  and with added inert gas. Secondly, Fig. 9 shows the dependence on  $[\text{O}_2]$  of the decay rates  $\gamma(k' - K)$  in the form of eqn. (4) for the removal of  $\text{Sb}(5^4\text{S}_{3/2})$  in the presence of  $\text{O}_2$  and He. Thirdly, Fig. 10 shows the clear kinetic dependence on the pressures of the third bodies He,  $\text{N}_2$  and  $\text{SF}_6$ . From these plots we obtained the absolute third order rate constants for the overall process



namely  $k_{\text{O}_2}^{\text{M}}$  ( $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ ) has the value  $2.2 \pm 0.2 \times 10^{-31}$  for  $\text{M} = \text{He}$ ,  $3.2 \pm 0.3 \times 10^{-31}$  for  $\text{M} = \text{N}_2$  and  $3.6 \pm 0.4 \times 10^{-31}$  for  $\text{M} = \text{SF}_6$ . These data indicate that the lifetimes of the energised intermediate  $\text{SbO}_2^*$  are of the order of  $10^{-11}$  s. Bimolecular atom transfer would, of course, be endothermic:

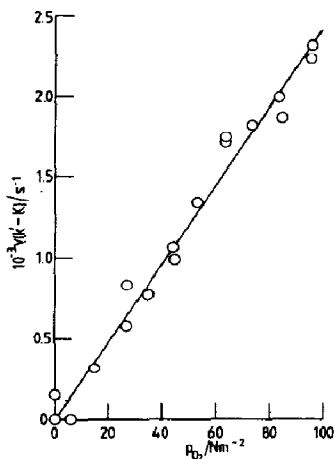


Fig. 9. Pseudo first order rate coefficients  $\gamma(k' - K)$  for the decay of  $\text{Sb}(5^4\text{S}_{3/2})$  in the presence of oxygen and helium.  $p_{\text{SbMe}_3} = 0.27 \text{ N m}^{-2}$ ,  $p_{\text{total with He}} = 5.3 \text{ kN m}^{-2}$ ;  $E = 360 \text{ J}$ .

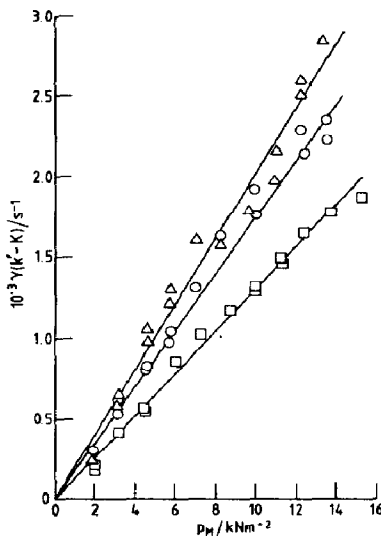
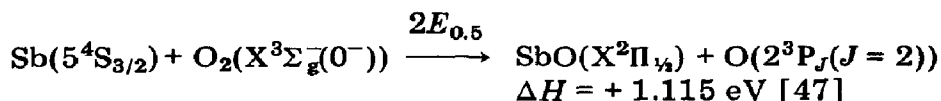
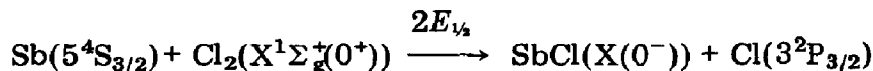
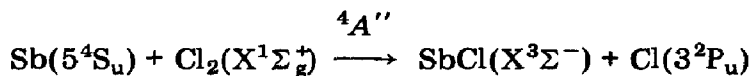


Fig. 10. Pseudo first order rate coefficients  $\gamma(k' - K)$  for the decay of  $\text{Sb}(5^4\text{S}_{3/2})$  in the presence of oxygen with different third bodies (M).  $p_{\text{SbMe}_3} = 0.27 \text{ N m}^{-2}$ ,  $p_{\text{O}_2} = 29 \text{ N m}^{-2}$ ;  $E = 360 \text{ J}$ ;  $\square$  He;  $\circ$   $\text{N}_2$ ;  $\triangle$   $\text{SF}_6$ .



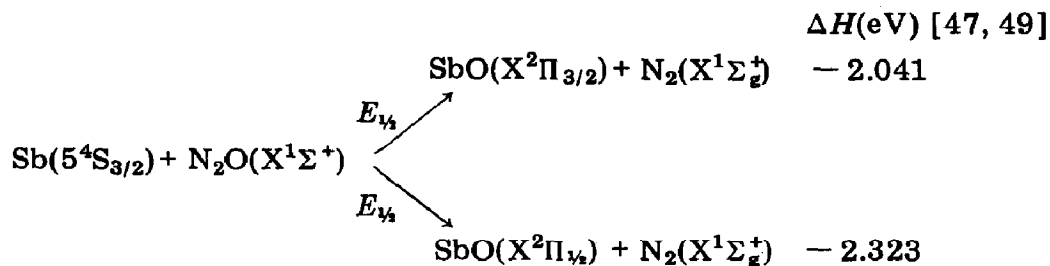
### $\text{Sb} + \text{Cl}_2, \text{N}_2\text{O}$

Unfortunately we were unable to measure the rate of the reaction between  $\text{Sb}(5^4\text{S}_{3/2})$  and  $\text{Cl}_2$  which correlates exothermically ( $\Delta H = -1.22 \text{ eV}$  [47, 48]) with ground state products on the basis of both weak spin orbit coupling and ( $J, \Omega$ ) coupling:



following the suggested assignment of  $\text{SbCl}(\text{X}^3\Sigma^-(0^-,1))$  given by Rosen [48]. Although low pressures of both  $\text{SbMe}_3$  and  $\text{Cl}_2$  were employed, reaction between these molecules, as measured by the resulting relative concentrations and lifetimes of  $\text{Sb}(5^4\text{S}_{3/2})$  in these experiments, was too fast to permit the study of  $\text{Sb} + \text{Cl}_2$  by the present method.

As with  $\text{Bi} + \text{N}_2\text{O}$ , the kinetic results for  $\text{Sb} + \text{N}_2\text{O}$  were confusing. Oxygen atom abstraction would arise from symmetry-allowed exothermic routes on the basis of ( $J, \Omega$ ) coupling:



(The states of SbO are designated according to Rosen [48].) We were unable to stimulate measurable decays at room temperature and can only infer a lower limit for  $k(\text{Sb} + \text{N}_2\text{O}) \leq 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (room temperature). At elevated temperatures ( $T = 373 - 473 \text{ K}$ ), good first order kinetic decays were found for  $\text{Sb}(5^4S_{3/2})$  and  $\gamma(k' - K)$  showed a good linear dependence on  $[\text{N}_2\text{O}]$ . Plotting these data in the standard Arrhenius form yielded  $k_{\text{N}_2\text{O}} = 2 \times 10^{-15} \exp(-2 \text{ kJ}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Although these data are consistent with the concluded room temperature limit they portray a surprisingly low activation energy for the reaction, bearing in mind the linear closed shell structure of  $\text{N}_2\text{O}$ . Further, the pre-exponential factor is also small for what would be the combined effect of two symmetry-allowed processes. Wiesenfeld and Yuen [50] have measured the overall rate for the reaction of  $\text{Sn} + \text{N}_2\text{O}$  and have obtained  $k(\text{Sn} + \text{N}_2\text{O}) = (5.0 \pm 1.0) \times 10^{-13} \exp\{-(16.7 \pm 0.8)\text{kJ}/RT\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . These data have been attributed to non-adiabatic transitions based on the weak spin orbit coupling approximation leading to electronically excited products. Applying weak spin orbit coupling to this system, the reaction between  $\text{Sb} + \text{N}_2\text{O}$  to yield ground state  $\text{SbO} + \text{N}_2$  would also be symmetry-disallowed (*i.e.* spin-forbidden). However, the spin orbit splittings in atomic Sb and molecular SbO are clearly large and we assume that ( $J, \Omega$ ) coupling must operate.

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