

KINETIC STUDY OF GROUND STATE BISMUTH ATOMS, $\text{Bi}(6^4\text{S}_{3/2})$, BY TIME-RESOLVED ATTENUATION OF ATOMIC RESONANCE RADIATION

D. HUSAIN and N. K. H. SLATER

Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP (Gt. Britain)

(Received October 1, 1976)

Summary

A kinetic study of ground state bismuth atoms, $\text{Bi}(6^4\text{S}_{3/2})$, is described. The Bi atoms were generated by the pulsed irradiation of low pressures of BiMe_3 and monitored photoelectrically in absorption in the "single-shot" mode by time-resolved attenuation of atomic resonance radiation at $\lambda = 306.77 \text{ nm}$ ($7^4\text{P}_{1/2} \leftarrow 6^4\text{S}_{3/2}$). The decay of the atom was investigated in the presence of a number of reactant gases, namely C_2H_4 , C_2H_2 , NO , O_2 and N_2O , in the presence of various buffer gases (He , N_2 , SF_6), and, in some cases, over a temperature range up to $\sim 600 \text{ K}$. Removal in the presence of C_2H_4 and of C_2H_2 showed third order kinetics and yielded the following absolute rate constants (293 K):

$\text{Bi} + \text{C}_2\text{H}_4 + \text{M}$	
M	$k_{\text{C}_2\text{H}_4}^{\text{M}}$ ($\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$)
He	$3.1 \pm 0.2 \times 10^{-33}$
N_2	$8.2 \pm 0.7 \times 10^{-33}$
SF_6	$1.8 \pm 0.1 \times 10^{-32}$

$\text{Bi} + \text{C}_2\text{H}_2 + \text{M}$	
M	$k_{\text{C}_2\text{H}_2}^{\text{M}}$ ($\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$)
He	$1.1 \pm 0.1 \times 10^{-33}$
N_2	$7.4 \pm 0.2 \times 10^{-33}$
SF_6	$6.5 \pm 0.4 \times 10^{-33}$

Removal in the presence of $\text{C}_2\text{H}_4 + \text{He}$ yielded the Arrhenius parameters:

$$k_{\text{C}_2\text{H}_4}^{\text{He}} = 1.6 \pm 0.1 \times 10^{-32} \exp\left(-\frac{4.0 \pm 0.4 \text{ kJ/mol}}{RT}\right) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}.$$

The kinetics in $C_2H_2 + He$ also included a significant, diffusion controlled component in the decay of $Bi(6^4S_{3/2})$. Removal by NO showed second-order kinetics, yielding the same rate constant in the presence of the gases He, N_2 and SF_6 of $k_{NO} = 5.6 \pm 0.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (293 K). The kinetic decays in the presence of O_2 and of N_2O were found to be complex.

Introduction

There have been a number of direct kinetic investigations on various atoms in group V in specific electronic states arising from the overall np^3 ground state electronic configuration [1, 2]. Whilst ground state nitrogen atoms, $N(2^4S_{3/2})$, have been the object of special attention on account of their importance in the chemistry of the upper atmosphere [3], involving a variety of marker techniques [4 - 9] but also including direct monitoring via the atomic absorption spectrum in the vacuum ultra-violet [10, 11], there has been little work on the remaining atoms in the ground state. Direct investigation of the collisional behaviour of the atoms $N \rightarrow Bi$ has been concerned principally with the optically metastable $np^3(^2D_J)$ and $np^3(^2P_J)$ states. Thus, rate data have been reported for $N(2^2D_J, 2^2P_J)$ [11 - 13], $P(3^2D_J, 3^2P_J)$ [14 - 16], $As(4^2D_J, 4^2P_J)$ [17 - 19], $Sb(5^2D_{3/2,5/2})$ [20] and $Bi(6^2D_{3/2,5/2})$ [21]. Very recently, Husain and Norris [22] have reported a detailed kinetic method for monitoring $P(3^4S_{3/2})$ by atomic absorption spectroscopy in the vacuum ultra-violet and have given some collisional rate data for this atomic state. The overall objective of much of this work in group V has been to investigate the relationship between reactivity and electronic structure, using the weak spin orbit coupling approximation to discuss the nature of the potential surfaces for light atom-molecule collisions [23, 24] and (J, Ω) coupling for heavy atom-molecule collisions [21, 25].

In this paper, we describe rate measurements on ground state bismuth atoms, $Bi[6p^3(^4S_{3/2})]$, generated by pulsed irradiation and monitored by attenuation of atomic resonance radiation in the ultra-violet. To the best of our knowledge, there are no previous rate data for this atomic state derived from direct monitoring of the atom. As well as the interest in investigating the kinetic behaviour of the heavy atoms in order to study the effect of strong spin orbit coupling on collisions, there is also a growing interest in heavy atom collisions from the viewpoint of possible chemical laser systems in the visible region of the spectrum resulting from molecular electronic transitions [26 - 28].

Experimental

The experimental arrangement was essentially that described by Bevan and Husain for the study of $Bi(6^2D_{3/2})$ and $Bi(6^2D_{5/2})$ [21] with some modi-

fications. $\text{Bi}(6^4\text{S}_{3/2})$ was generated by the low energy pulsed irradiation ($E = 101 \text{ J}$, $2.5 \mu\text{F}$, 9 kV) of low pressures of bismuth trimethyl, BiMe_3 , in the presence of excess helium buffer gas to ensure no significant temperature rise above ambient conditions on photolysis. Typically, $p_{\text{He}}:p_{\text{BiMe}_3} = \sim 100,000:1$. The reactor system, unlike that of previous measurements on $\text{Bi}(6^2\text{D}_{3/2})$ and $\text{Bi}(6^2\text{D}_{5/2})$ [21], did not involve a coaxial lamp and vessel assembly but a standard, separate flash lamp and reaction vessel. These were constructed of high purity quartz (Spectrosil) which, in air optics, limited photolysis to $\lambda > \sim 185 \text{ nm}$. A furnace with a standard electrical winding was used to heat the lamp and the reaction system up to $\sim 185 \text{ nm}$. A furnace with a standard electrical winding was used to heat the lamp and the reaction system up to $\sim 600 \text{ K}$, measured with a thermocouple.

Following pulsed irradiation, $\text{Bi}(6^4\text{S}_{3/2})$ was monitored photoelectrically in absorption by time-resolved attenuation of resonance radiation from a microwave-powered atomic flow lamp ($p_{\text{BiMe}_3} = 1.3 \text{ N/m}^2$, $p_{\text{total with He}} = 133 \text{ N/m}^2$; incident power = 100 W). Whilst kinetic measurements were restricted to the ground state, the three following resonance transitions were employed, including two for the $6^2\text{D}_{3/2}$ and $6^2\text{D}_{5/2}$ states, in order to investigate the possible production of these optically metastable species [29] on photolysis in this system:

Transition	$\lambda(\text{nm})$ [30]	$10^{-8} \times gA(\text{s}^{-1})$ [30]
$7^4\text{P}_{1/2} \rightarrow 6^4\text{S}_{3/2}$	306.77	7.0
$7^2\text{P}_{1/2} \rightarrow 6^2\text{D}_{3/2}$	289.80	32
$7^4\text{P}_{5/2} \rightarrow 6^2\text{D}_{5/2}$	302.46	38

Notwithstanding the lower transition probability for the ground state line, it is observed to be the most intense atomic transition in the spectrum [31]. The attenuated resonance radiation was detected by means of a photomultiplier (E.M.I. 9783B) mounted on the exit slit of a Seya-Namioka grating monochromator [18]. The transient signals, representing light absorption by the bismuth atoms, were amplified with a now standard current-to-voltage convertor employing a fast-settling operational amplifier [32] to avoid signal distortion. The signals were then transferred directly to a transient recorder (Data Laboratories DL 905), where they were digitized and stored, and subsequently punched onto paper tape in ASCII code (Datadynamics punch 1133) for direct input into the University's computer (IBM 370).

As with the experiments on $\text{Bi}(6^2\text{D}_{3/2,5/2})$ [21], we did not employ a modified Beer-Lambert law [33]:

$$I_{\text{tr}} = I_0 \exp[-\epsilon(cl)^\gamma] \quad (\text{i})$$

as we do not consider the accuracy in the intercepts of the first-order kinetic plots (see later) justified the determination of γ by the standard procedure [33]. Furthermore, this procedure [33] would require, in this case, accurate

dispensing and measurement of pressures of BiMe_3 in the region of 10^{-4} Torr (1 Torr = 133 N/m^2). The experiments employed the Beer–Lambert law directly:

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

Of course, any departure from this law due to an effective, constant value of γ , would affect the measured value of a rate constant directly since the slope of a first-order kinetic plot, *i.e.* $\ln c \equiv \ln[\ln(I_0/I_{\text{tr}})]$ vs. t , is given by $-\gamma k'$ according to eqn. (i), where k' is the overall first-order decay coefficient for $\text{Bi}(6^4\text{S}_{3/2})$. Furthermore, calculation of the “curve-of-growth” [34], *i.e.* the relationship between I_{tr}/I_0 and the Bi particle density, in order to estimate any departure from the Beer–Lambert law, would be extremely complex. The use of idealized line shapes and specific layer models in such calculations are established [35 - 44]. However, this system would require extensive computation to allow for the effect of nuclear hyperfine interaction as described for halogen atom transitions by Tellinghuisen and Clyne [56] and, more recently, for the transition $\text{P}[4s(4^4\text{P}_{5/2}) - 3p^3(4^4\text{S}_{3/2})]$ at $\lambda = 177.50 \text{ nm}$ by Husain and Norris [22]. The high nuclear spin of the bismuth atom ($I = 9/2$) [46] would require nuclear hyperfine splittings arising from the interaction of the nuclear electric quadrupole moment with the electric field gradient at nucleus and the nuclear magnetic dipole moment with the magnetic field, as well as higher order terms, to be included in the line shapes. On the basis of the simple vector model [47] and the standard selection rules ($\Delta F = 0, \pm 1$ [47]), the calculation would involve summation over the integrals for six lines in the case of the $7^4\text{P}_{1/2} - 6^4\text{S}_{3/2}$ transition of the Bi atom. As a reasonable assumption, we will take $\gamma = 1$ for the present kinetic purposes. The calculations on the $\text{P}[4s(4^4\text{P}_{5/2}) - 3p^3(4^4\text{S}_{3/2})]$ [22] transition showed that the Beer–Lambert law ($\gamma = 1$) would still be expected to be obeyed in the range of atomic particle densities employed in this type of experiment though with less sensitivity when nuclear hyperfine interactions are included. We may recognize that any small departures from the Beer–Lambert law as described in eqn. (ii) will affect the absolute magnitudes of rate constants as described.

Materials

He, Kr (for the photoflash lamp), N_2 , O_2 , N_2O , C_2H_4 and BiMe_3 were prepared as described by Bevan and Husain [21]. NO , C_2H_2 and SF_6 were taken from cylinders and purified, where necessary, essentially as described hitherto [12, 16, 25].

Results and Discussion

Bi + ethylene

Figure 1 shows a typical plot of the computerized output of the digitized time-variation of the transmitted intensity at $\lambda = 306.77 \text{ nm}$, indicating the

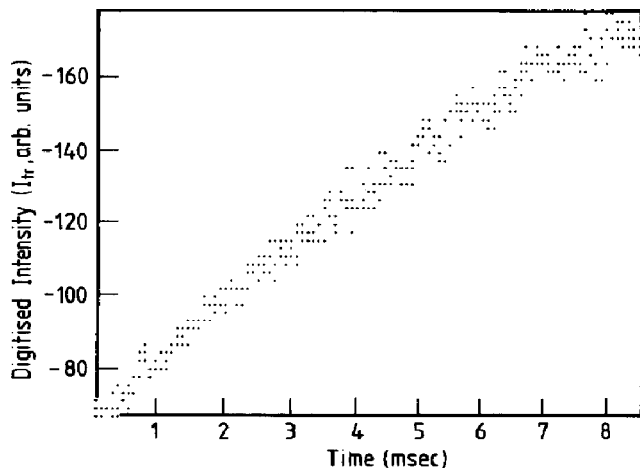


Fig. 1. Digitised time-variation of the transmitted light intensity at $\lambda = 306.77$ nm $\text{Bi}(7^4\text{P}_{1/2}) \rightarrow \text{Bi}(6^4\text{S}_{3/2})$ indicating the decay of resonance absorption by $\text{Bi}(6^4\text{S}_{3/2})$ in the presence of ethylene; $p_{\text{BiMe}_3} = 0.40 \text{ N m}^{-2}$, $p_{\text{C}_2\text{H}_4} = 21 \text{ N m}^{-2}$, $p_{\text{total with He}} = 5.3 \text{ kN m}^{-2}$; $E = 101 \text{ J}$; $T = 293 \text{ K}$.

decay of resonance absorption by $\text{Bi}(6^4\text{S}_{3/2})$ in the presence of ethylene. Before proceeding with the kinetic analysis for the ground state atoms, transient absorption at $\lambda = 289.80$ and 302.46 nm (see experimental) was investigated in order to ascertain if any significant quantities of $\text{Bi}(6^2\text{D}_{3/2})$ or $\text{Bi}(6^2\text{D}_{5/2})$ were generated in these experiments with the accompanying kinetic effects on $\text{Bi}(6^4\text{S}_{3/2})$. As may be expected for the low energy employed in this system ($E = 101 \text{ J}$) compared with that used on the previous measurements on these metastable states [21] which were further carried out in a coaxial reactor and vessel assembly ($\lambda > \sim 165 \text{ nm}$), $\text{Bi}(6^2\text{D}_J)$ was not detected in any of the present studies. It was necessary, as again might be expected, to employ low pressures of BiMe_3 ($\sim 10^{-4}$ Torr) in order to prevent saturation of the $\lambda = 306.77$ nm resonance line for long periods of time ($\sim 3 \text{ ms}$), restricting kinetic analyses to the tail of the decay. The magnitude of the unattenuated signal, I_0 , was determined by employing the two time bases of the transient recorder. This permitted separation of the recorder trace into two regions: (i) 824 points of the 1024 point memory were recorded for analysis of the transient signal; (ii) the remaining 200 points were recorded over a period of one second in order to determine the I_0 value individually for each trace. Hence, by contrast with the earlier measurements on $\text{Bi}(6^2\text{D}_J)$ [21], the effective time over which the signal is averaged in order to obtain the I_0 value is independent of the sweep time used to monitor the kinetic decay and is constant from one trace to another. We may note that in the absence of a reactant gas, using only $\text{BiMe}_3 + \text{He}$, the lifetime of $\text{Bi}(6^4\text{S}_{3/2})$ is long, $\sim 30 \text{ ms}$, with a complex shape representing both first-order kinetics, including diffusion, together with removal by atomic recombination.

Figure 2 shows the computerized first-order kinetic plots for the decay of $\text{Bi}(6^4\text{S}_{3/2})$ in the presence of different pressures of ethylene, Fig. 2(a)

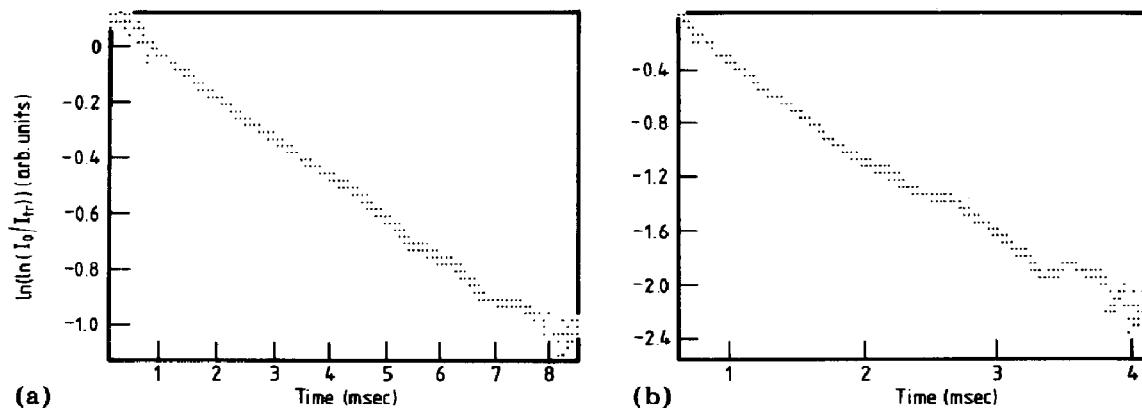


Fig. 2. Typical pseudo first-order plots for the decay of $\text{Bi}(6^4\text{S}_{3/2})$ in the presence of ethylene, obtained by monitoring the absorption of light at $\lambda = 306.77 \text{ nm}$ ($\text{Bi}(7^4\text{P}_{1/2}) \leftarrow \text{Bi}(6^4\text{S}_{3/2})$) $p_{\text{BiMe}_3} = 0.40 \text{ N m}^{-2}$, $p_{\text{total with He}} = 5.3 \text{ kN m}^{-2}$; $E = 101 \text{ J}$; $T = 293 \text{ K}$; $p_{\text{C}_2\text{H}_4} (\text{N m}^{-2})$: (a) 21 (b) 338.

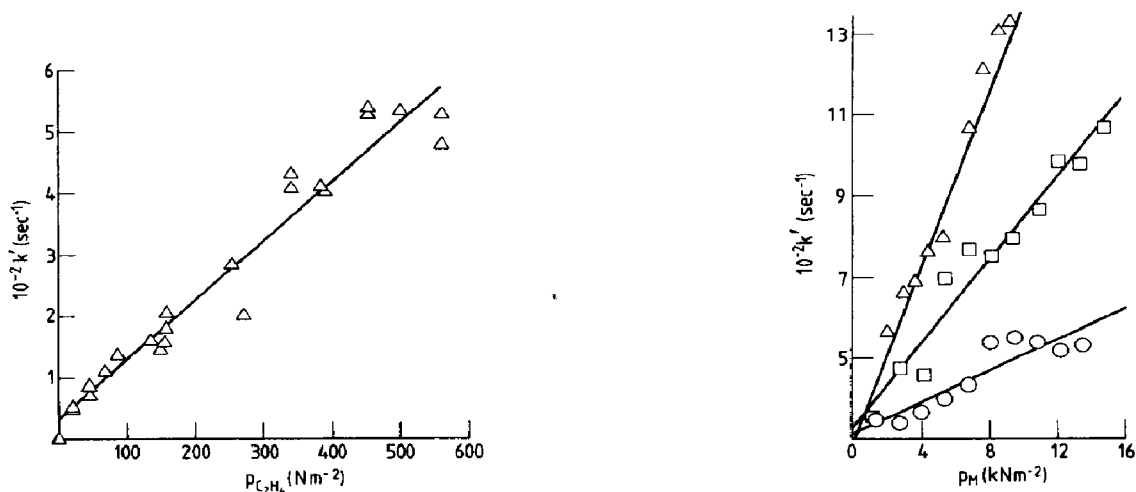


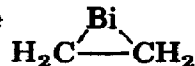
Fig. 3. Pseudo first-order rate coefficients (k') for the decay of $\text{Bi}(6^4\text{S}_{3/2})$ in the presence of ethylene; $p_{\text{BiMe}_3} = 0.40 \text{ N m}^{-2}$, $p_{\text{total with He}} = 5.3 \text{ kN m}^{-2}$; $E = 101 \text{ J}$; $T = 293 \text{ K}$.

Fig. 4. Pseudo first-order rate coefficients (k') for the decay of $\text{Bi}(6^4\text{S}_{3/2})$ in the presence of ethylene with different third bodies (M); $p_{\text{BiMe}_3} = 0.40 \text{ N m}^{-2}$, $p_{\text{C}_2\text{H}_4} = 400 \text{ N m}^{-2}$; $E = 101 \text{ J}$; $T = 293 \text{ K}$; \circ He; \square N_2 ; \triangle SF_6 .

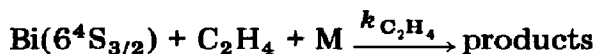
representing analysis of the raw data given in Fig. 1. The data-smoothing procedure of Savitsky and Golay [48] was employed. Figure 3 shows a plot of the first-order decay coefficient, k' , derived from the slopes of the plots of the type given in Fig. 2 as a function of the pressure of C_2H_4 . This graph is drawn, in this instance, directly over the computerized output for this plot, derived in the computer from the raw data for I_{tr} vs. t on paper tape. The plot (Fig. 3) describes the first-order removal of $\text{Bi}(6^4\text{S}_{3/2})$ in the form:

$$k' = K + k_R [R] \quad (\text{iii})$$

where K is taken to be a constant in a series of kinetic runs in which only the reactant, $[R]$, is varied. k_R is the second order rate coefficient, not necessarily a constant. In fact, having established the first-order dependence on both $[\text{Bi}(6^4\text{S}_{3/2})]$ and on $[\text{C}_2\text{H}_4]$, the kinetics were found to be third-order overall. Figure 4 shows the variation of k' with three third bodies, He, N_2 and SF_6 . The data for helium are somewhat scattered but the kinetic effect is clear, presumably representing stabilization of the



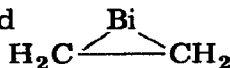
intermediate. The data of Fig. 4 combined with the kinetic plots of the type given in Fig. 3 yield the overall third-order rate constants for the process:



at room temperature (20 °C) of:

M	$k_{\text{C}_2\text{H}_4}$ (cm ⁶ molecule ⁻² s ⁻¹)
He	$3.1 \pm 0.2 \times 10^{-33}$
N_2	$8.2 \pm 0.7 \times 10^{-33}$
SF_6	$1.8 \pm 0.1 \times 10^{-32}$

A simple mechanism based on bimolecular reactions with stabilization of the energized



such a species is only $\sim 10^{-13}$ s, which is short for a polyatomic species of this size. The relative efficiencies of He, N_2 and SF_6 are in sensible accord with those observed in atomic recombination [49, 50]. A small positive temperature dependence is observed for the process $\text{Bi} + \text{C}_2\text{H}_4 + \text{He} \rightarrow \text{products}$, the Arrhenius plot for which is given in Fig. 5. This yields

$$k_{\text{C}_2\text{H}_4}^{\text{He}} = 1.6 \pm 0.1 \times 10^{-32} \exp\left(-\frac{4.0 \pm 0.4 \text{ kJ/mol}}{RT}\right)$$

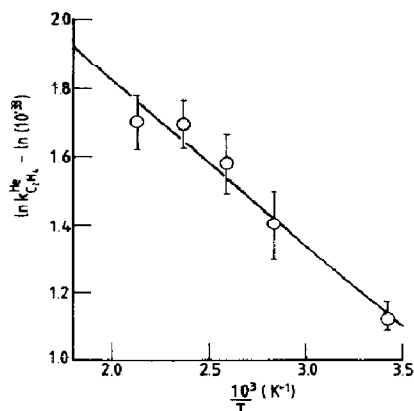


Fig. 5. Arrhenius plot for the decay of $\text{Bi}(6^4\text{S}_{3/2})$ in the presence of ethylene and helium.

$\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$. The addition of group VI atoms (O, S, Se, Te) in their 3P_J ground states to ethylene has been studied in detail in the past [51 - 54], the addition generally exhibiting small positive temperature coefficients of the order of magnitude of that observed here for the Bi atom. Whilst ground state nitrogen atoms have been reacted with C_2H_4 in discharge flow systems, we hesitate to include a discussion of an activation energy for the addition reaction which is difficult to extract from a system involving a complex chain reaction [55]. There are no analogous data for the remaining group V atoms.

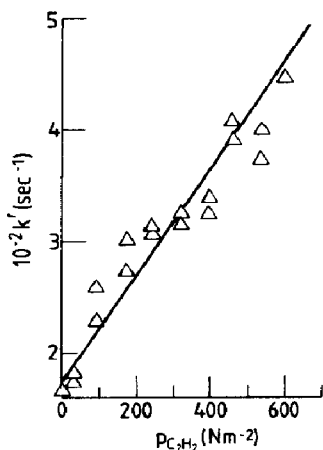


Fig. 6. Pseudo first-order rate coefficients (k') for the decay of $\text{Bi}(6^4\text{S}_{3/2})$ in the presence of acetylene; $p_{\text{BiMe}_3} = 0.40 \text{ N m}^{-2}$, $p_{\text{total with He}} = 5.3 \text{ kN m}^{-2}$; $E = 101 \text{ J}$.

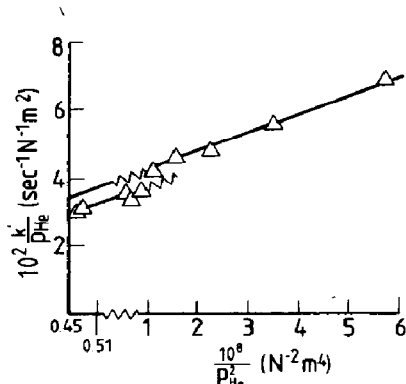


Fig. 7. Decay of $\text{Bi}(6^4\text{S}_{3/2})$ in the presence of acetylene and helium. Estimation of contribution by diffusion-controlled decay by employing the relationship $k' = a[\text{He}] + b/[\text{He}]$ $p_{\text{BiMe}_3} = 0.40 \text{ N m}^{-2}$, $p_{\text{C}_2\text{H}_2} = 400 \text{ N m}^{-2}$; $E = 101 \text{ J}$.

Bi + acetylene

Similar results to those obtained for C_2H_4 were observed for the decay of $\text{Bi}(6^4\text{S}_{3/2})$ in the presence of acetylene, with the modification that some curvature was observed in the first-order plots at longer times in the higher pressures of helium employed and, in a number of such cases, the first-order decay coefficient was taken from the initial slope. Figure 6 shows the dependence of k' with the pressure of C_2H_2 at a fixed pressure of helium. The relatively slow rates in He at higher pressures led us to *estimate* the contribution to the decay from diffusion. Approximating the decay coefficient to two contributions, namely, third-order removal by $\text{C}_2\text{H}_2 + \text{He}$ and diffusional removal, then at a given pressure of C_2H_2 , k' can be written in the form:

$$k' = a [\text{He}] + b / [\text{He}] \quad (\text{iv})$$

Here $a = k_{\text{C}_2\text{H}_2}^{\text{He}} [\text{C}_2\text{H}_2]$ and b can approximately taken from the "long-time" solution of the diffusion equation for a cylinder, generally written in the form of the diffusional decay coefficient, β , given by [56]:

$$\beta = \left(\frac{\Pi^2}{l^2} + \frac{2.41^2}{r^2} \right) D_{12} \quad (\text{v})$$

where D_{12} is the diffusion coefficient, in this case, of Bi in He. Figure 7 shows the data for the decay of $\text{Bi}(6^4\text{S}_{3/2})$ in the presence of $\text{C}_2\text{H}_2 + \text{He}$ in the rearranged form of eqn. (iv). This plot yields $D_{\text{Bi-He}} \cong 1.1 \text{ cm}^2/\text{s}$ at one atmosphere and a value for $k_{\text{C}_2\text{H}_2}^{\text{He}}$ ($1.3 \pm 0.1 \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, 293 K) in sensible accord with the value simply taken from the slope of Fig. 6 ($k_{\text{C}_2\text{H}_2}^{\text{He}} = 1.5 \pm 0.2 \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$). If we take the plot of k' versus p_{He} and make the appropriate approximate correction for diffusion using the above value for $D_{\text{Bi-He}}$, we obtain the value for $k_{\text{C}_2\text{H}_2}^{\text{He}}$, which we report, together with the appropriate data for N_2 and SF_6 taken from the plots in Fig. 8, namely:

M	$k_{\text{C}_2\text{H}_2}$ ($\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$)
He	$1.1 \pm 0.1 \times 10^{-33}$
N_2	$7.4 \pm 0.2 \times 10^{-33}$
SF_6	$6.5 \pm 0.4 \times 10^{-33}$

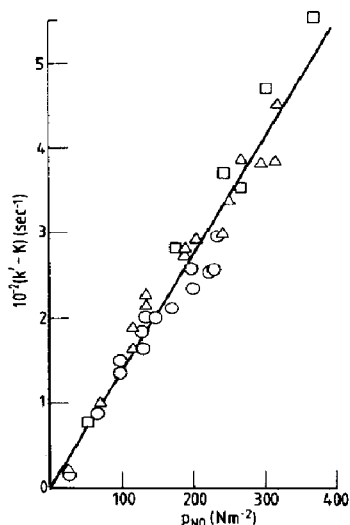
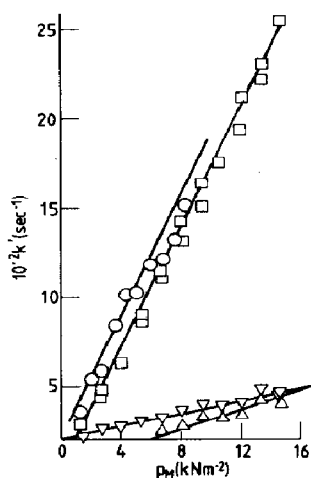


Fig. 8. Pseudo first-order rate coefficients (k') for the decay of $\text{Bi}(6^4\text{S}_{3/2})$ in the presence of acetylene with different third bodies (M); $p_{\text{BiMe}_3} = 0.40 \text{ N m}^{-2}$, $p_{\text{C}_2\text{H}_2} = 400 \text{ N m}^{-2}$; $E = 101 \text{ J}$; ∇ He, not corrected for diffusion; \triangle He, diffusion corrected; \square N_2 ; \circ SF_6 .

Fig. 9. Pseudo first-order rate coefficients (k') for the decay of $\text{Bi}(6^4\text{S}_{3/2})$ in the presence of nitric oxide and He, N_2 and SF_6 ; $p_{\text{BiMe}_3} = 0.40 \text{ N m}^{-2}$, $p_{\text{He}, \text{N}_2, \text{SF}_6} = 5.3 \text{ kN m}^{-2}$; $E = 101 \text{ J}$; \square He; \triangle N_2 ; \circ SF_6 .

Bi + nitric oxide

The decay of $\text{Bi}(6^4\text{S}_{3/2})$ in the presence of nitric oxide did not show third-order kinetics. Figure 9 shows the rate data for the removal of the atom in the presence of the three gases (He, N_2 and SF_6) on one plot. Taken separately as second order rate data for $\text{Bi} + \text{NO}$, the results yielded the

following absolute rate constants: k (in He) = $5.6 \pm 0.4 \times 10^{-14}$, k (in SF₆) = $5.1 \pm 0.4 \times 10^{-14}$ and k (in N₂) = $5.6 \pm 0.3 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹.

Taking all the data in Fig. 9, we report for:



$k_{\text{NO}} = 5.6 \pm 0.1 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ (293 K). Clearly, reaction to yield BiO + N would be highly endothermic ($\Delta H = +3.4$ eV [57, 58]). The second-order kinetics would indicate a strong intermediate.

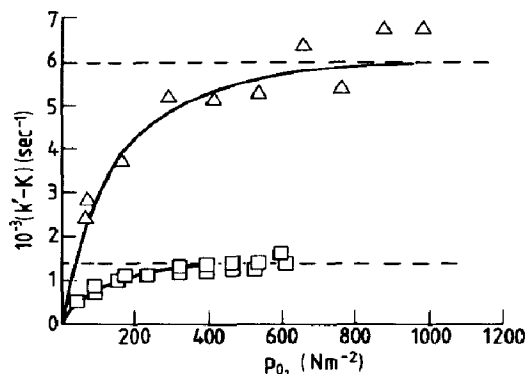


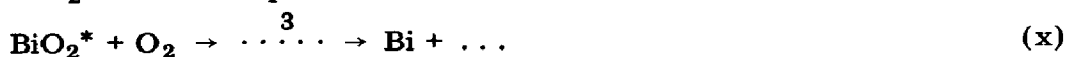
Fig. 10. Pseudo first-order rate coefficients (k') for the decay of Bi($6^4S_{3/2}$) in the presence of O₂; $p_{\text{BiMe}_3} = 0.40$ N m⁻²; $E = 101$ J; $p_{\text{total with He}}$ (kN m⁻²): □ 5.3; △ 26.6.

Bi + oxygen, nitrous oxide

The kinetic results for the decay of Bi($6^4S_{3/2}$) were too complex for a detailed analysis with O₂ and N₂O. Sensible first-order decays were observed for Bi($6^4S_{3/2}$) in the presence of both O₂ and N₂O. The former, however, yielded a complex dependence on [O₂] which is shown in Fig. 10 at two pressures of helium differing by a factor of 5. The full curves represent arbitrary computerized fitting of the data to the form:

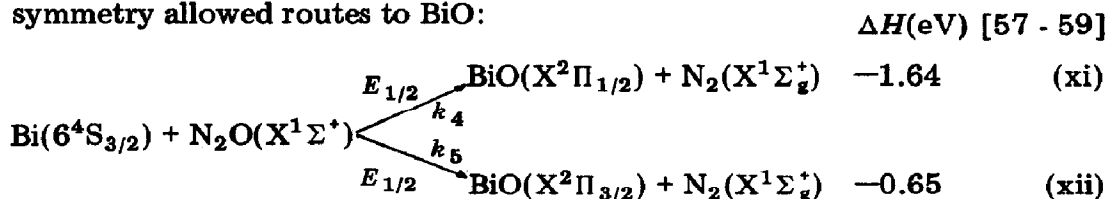
$$(k' - K) = c(1 - e^{-d[\text{O}_2]}) \quad (\text{vii})$$

in order to determine the decay rate which becomes independent of [O₂] at infinite O₂ pressure. This yielded $(k' - K)$ ($p_{\text{O}_2} = \infty, p_{\text{He}} = 5.3$ kN/m²) = 1.4×10^3 and $(k' - K)$ ($p_{\text{O}_2} = \infty, p_{\text{He}} = 26.6$ kN/m²) = 6.0×10^3 s⁻¹, in sensible agreement within the bounds of measurement, with the ratio of inert gas pressures. Clearly, reaction to yield BiO + O would be highly endothermic ($\Delta H = 1.7$ eV [58, 59]). There is certainly no rôle played by either of the ²D states (see earlier). One could write a general formal mechanism of the type:



which would yield a rate independent of $[O_2]$ if the effective value of $k_3[O_2] \gg (k_{-1} + k_2[He])$. However, further consideration of this reaction is not justified from observation of the single variable, $Bi(6^4S_{3/2})$. The initial slopes in Fig. 10 yielded an estimate of an effective third order rate constant of $k_{O_2}^{H_e} = \sim 3 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$.

The slow rates observed here with N_2O were especially disappointing as the correlation diagram in (J, Ω) coupling, assuming C_s symmetry on collision, and which has been given hitherto [21], clearly shows exothermic and symmetry allowed routes to BiO :



We may estimate a lower limit from the observed data of $k_4 + k_5 < 2.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (320 K) though this estimate is of limited use as we consider that the reaction is characterized by a large energy barrier. This type of behaviour has been found hitherto for a large number of atomic abstraction reactions with N_2O [1, 2] which are exothermic and for which there are direct potential surfaces. This energy barrier is presumed to arise from the linear closed shell structure of N_2O . The temperature was varied over 300 K with the rate showing a maximum at $T = 340 \text{ K}$ from which we could only estimate $k_4 + k_5 < 3.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (340 K). The rate, however, exhibited no simple dependence with temperature, presumably as a result of the thermal decomposition of N_2O and reaction with the parent $BiMe_3$. Clearly, investigation of this type of reaction will require an experimental arrangement involving a high temperature, fast flow system.

Acknowledgement

We thank the Science Research Council of Great Britain for a Research Studentship to one of us (N. K. H. S.) during the tenure of which this work was carried out.

References

- 1 R. J. Donovan and D. Husain, *A. Rep. Chem. Soc.*, 68A (1971) 123.
- 2 R. J. Donovan, D. Husain and L. J. Kirsch, *A. Rep. Chem. Soc.*, 69A (1972) 19.
- 3 L. F. Phillips and M. J. McEwan, *Atmospheric Chemistry*, Edward Arnold, London (1975).
- 4 A. Nelson Wright and C. A. Winkler, *Active Nitrogen*, Academic Press, New York and London (1968).
- 5 I. M. Campbell and B. A. Thrush, *A. Rep. Chem. Soc.*, 62A (1965) 17.
- 6 B. Brocklehurst and K. R. Jennings, *Progr. React. Kinet.*, 4 (1967) 1.
- 7 G. G. Manella, *Chem. Rev.*, 63 (1963) 1.
- 8 K. R. Jennings and J. W. Linnett, *Q. Rev. Chem. Soc.*, 12 (1958) 116.
- 9 M. F. Golde and B. A. Thrush, *Rep. Progr. Phys.*, 36 (1973) 1285.
- 10 F. A. Morse and F. Kaufman, *J. Chem. Phys.*, 42 (1965) 1785.
- 11 C. L. Lin and F. Kaufman, *J. Chem. Phys.*, 55 (1971) 3760.

- 12 D. Husain, L. J. Kirsch and J. R. Wiesenfeld, *Disc. Faraday Soc.*, 53 (1972) 201.
- 13 D. Husain, S. K. Mitra and A. N. Young, *J. C. S. Faraday Trans. II*, 70 (1974) 1721.
- 14 A. U. Acuna, D. Husain and J. R. Wiesenfeld, *J. Chem. Phys.*, 58 (1973) 494.
- 15 A. U. Acuna, D. Husain and J. R. Wiesenfeld, *J. Chem. Phys.*, 58 (1973) 5272.
- 16 A. U. Acuna and D. Husain, *J. C. S. Faraday Trans. II*, 69 (1973) 585.
- 17 A. B. Callear and R. J. Oldman, *Trans. Faraday Soc.*, 64 (1968) 840.
- 18 M. J. Bevan and D. Husain, *J. Photochem.*, 3 (1974) 1.
- 19 M. J. Bevan and D. Husain, *Int. J. Chem. Kinet.*, 7 (1975) 63.
- 20 M. J. Bevan and D. Husain, *J. Photochem.*, 4 (1975) 51.
- 21 M. J. Bevan and D. Husain, *J. Phys. Chem.*, 80 (1976) 217.
- 22 D. Husain and P. E. Norris, *J. C. S. Faraday Trans. II* (1976) submitted.
- 23 R. J. Donovan and D. Husain, *Chem. Rev.*, 70 (1970) 489.
- 24 K. E. Shuler, *J. Chem. Phys.*, 21 (1953) 624.
- 25 A. Brown and D. Husain, *J. C. S. Faraday Trans. II*, 71 (1975) 699.
- 26 R. S. Bradford Jr., C. R. Jones, L. A. Southall and H. P. Broida, *J. Chem. Phys.*, 62 (1975) 2060.
- 27 G. A. Capelle, H. P. Broida and R. W. Field, *J. Chem. Phys.*, 62 (1975) 3131.
- 28 D. J. Eckstrom, S. A. Edelstein, D. L. Huestis and S. W. Benson, *J. Chem. Phys.*, 63 (1975) 3828.
- 29 R. H. Garstang, *J. Res. Nat. Bur. Stand.*, A68 (1964) 61.
- 30 C. H. Corliss and W. R. Bozman, *U.S. Nat. Bur. Stand., Monogr. No. 53*, (1962).
- 31 M. J. Bevan, Ph. D. Thesis, University of Cambridge (1975).
- 32 W. H. Wing and T. M. Sanders, Jr., *Rev. Sci. Instrum.*, 38 (1962) 1341.
- 33 R. J. Donovan, D. Husain and L. J. Kirsch, *Trans. Faraday Soc.*, 66 (1970) 2551.
- 34 A. C. G. Mitchell and M. W. Zemansky, *Resonance radiation and excited atoms*, Cambridge University Press, London (1934).
- 35 W. Bleeker, *Z. Phys.*, 52 (1929) 808.
- 36 R. W. Cowan and G. H. Dieke, *Rev. Mod. Phys.*, 20 (1948) 418.
- 37 W. Braun, A. M. Bass and D. D. Davis, *J. Opt. Soc. Am.*, 60 (1970) 166.
- 38 W. Braun and T. Carrington, *J. Quant. Spectros. Radiat. Trans.*, 9 (1968) 1133.
- 39 F. Kaufman and D. Parkes, *Trans. Faraday Soc.*, 66 (1970) 1579.
- 40 A. B. Prag, C. E. Fairchild and K. C. Clark, *Phys. Rev.*, A137 (1964) 1358.
- 41 D. A. Parkes, L. F. Keiser and F. Kaufman, *Astrophys. J.*, 149 (1967) 217.
- 42 C-L. Lin, D. A. Parkes and F. Kaufman, *J. Chem. Phys.*, 53 (1970) 3896.
- 43 M. A. A. Clyne and L. J. Piper, *J. C. S. Faraday Trans. II*, (1976) in press.
- 44 M. A. A. Clyne and L. T. Townsend, *J. C. S. Faraday Trans. II*, 70 (1974) 1863.
- 45 J. Tellinghuisen and M. A. A. Clyne, *J. C. S. Faraday Trans. II*, 72 (1976) 783.
- 46 W. Gordy, W. V. Smith and R. F. Trambarulo, *Microwave Spectroscopy*, Dover, New York, (1966), p. 344.
- 47 C. H. Townes and A. L. Schalow, *Microwave Spectroscopy*, McGraw-Hill, New York (1955).
- 48 A. Savitsky and J. E. Golay, *Anal. Chem.*, 36 (1964) 1627.
- 49 K. E. Russell and J. Simons, *Proc. R. Soc.*, A217 (1953) 271.
- 50 G. Porter, *Disc. Faraday Soc.*, 33 (1962) 198.
- 51 R. Atkinson and R. J. Cvetanovic, *J. Chem. Phys.*, 56 (1972) 432.
- 52 R. J. Donovan, D. Husain, R. W. Fair, O. P. Strausz and H. E. Gunning, *Trans. Faraday Soc.*, 66 (1970) 1635.
- 53 A. B. Callear and W. J. R. Tyerman, *Trans. Faraday Soc.*, 62 (1966) 2760.
- 54 J. Connor, A. van Roodselaar, R. W. Fair and O. P. Strausz, *J. Am. Chem. Soc.*, 93 (1971) 560.
- 55 D. R. Safrany, *Progr. React. Kinet.*, 6 (1971) 1.
- 56 M. W. Zemansky, *Phys. Rev.*, 34 (1929) 213.
- 57 B. Rosen, *Spectroscopic data relative to diatomic molecules*, Clarendon Press, Oxford (1972).
- 58 A. G. Gaydon, *Dissociation energies and spectra of diatomic molecules*, Chapman and Hall, London (1968).
- 59 G. Herzberg, *Electronic spectra of Polyatomic Molecules*, Van Nostrand, New York (1966).