KINETIC STUDIES OF Bi($6\,^4S_{3/2}$) BY TIME-RESOLVED ATOMIC RESONANCE FLUORESCENCE
II: AN INVESTIGATION OF THE THIRD-ORDER REACTIONS Bi + O_2 + M AND Bi + NO + M (M $\equiv$ He, N_2 AND CF_4)

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Summary

Kinetic studies of the removal of ground state bismuth atoms Bi($6\,^4S_{3/2}$) with O_2 and NO are reported following measurements of time-resolved atomic resonance fluorescence at λ = 306.8 nm (Bi($7\,^4P_{1/2}$) $\rightarrow$ Bi($6\,^4S_{3/2}$) + $h\nu$) subsequent to the flash photolysis of Bi(CH_3)$_3$. These processes were investigated in the presence of the buffer gases He, N_2 and CF_4 where significant diffusional corrections were found necessary with the resonance fluorescence technique for the pressure ranges employed with these gases. Overall third-order kinetics were observed for both Bi + O_2 + M and Bi + NO + M (M $\equiv$ He, N_2 and CF_4) yielding the following absolute third-order rate constants k_3 (cm^6 molecule^{-2} s^{-1}) (300 K; errors, 2σ): k_3(Bi + O_2 + He) = (3.3 $\pm$ 0.3) $\times$ 10^{-32}; k_3(Bi + O_2 + N_2) = (8.9 $\pm$ 0.9) $\times$ 10^{-32}; k_3(Bi + O_2 + CF_4) = (1.3 $\pm$ 0.4) $\times$ 10^{-31}; k_3(Bi + NO + He) = (3.9 $\pm$ 0.4) $\times$ 10^{-33}; k_3(Bi + NO + N_2) = (1.3 $\pm$ 0.2) $\times$ 10^{-32}; k_3(Bi + NO + CF_4) = (2.7 $\pm$ 0.8) $\times$ 10^{-32}.

These data are compared, where possible, with results derived from resonance absorption measurements on Bi($6\,^4S_{3/2}$) and also with analogous processes for the atomic states Sb($5\,^4S_{3/2}$), Pb($6\,^3P_0$) and Sn($5\,^3P_0$).

1. Introduction

It has been demonstrated in recent years that a number of reactions of ground state metal atoms, particularly heavy atoms, show overall third-order kinetics in the presence of the molecules O_2 and NO. Time-resolved atomic resonance absorption spectroscopy following flash photolysis has been the main technique leading to absolute kinetic data describing these types of overall processes. The absolute third-order rate constants for the reaction between Pb($6\,^3P_0$) + O_2 + M have been characterized for a wide range of

third bodies using this method [1 - 3]. The reaction between $Sn(5\,^3P_0) + O_2$, which is exothermic for atom abstraction ($\Delta H = -0.29$ eV [4]) is, by contrast, kinetically second order [5, 6]. For the heavy group V elements, third-order rate data have been reported for $Sb(5\,^4S_{3/2}) + O_2 + M$ [7] where reaction to yield SbO is endothermic ($\Delta H < 0.73$ eV [4]) whereas reaction between $Bi(6\,^4S_{3/2}) + O_2$, which is also endothermic ($\Delta H = 1.63$ eV [4]) exhibited complex kinetic behaviour when investigated by time-resolved atomic resonance absorption spectroscopy [8]. In broader terms, we may also note recent extensive kinetic studies of the third-order reactions of the ground state alkali elements (Li, Na, K) + O_2 + M [9 - 11]. For the group IV elements, both $Pb(6\,^3P_0)$ and $Sn(5\,^3P_0)$ were found to be described by overall third-order kinetics with NO, and a number of absolute rate constants were characterized [1, 6]. Second-order rate data have been reported for the removal of both $Bi(6\,^4S_{3/2})$ and $Sb(5\,^4S_{3/2})$ by NO from resonance absorption measurements [7, 8] despite reaction endothermicity in both cases [4].

In the preceding paper [12] we have given details of an experimental method for the kinetic investigation of $Bi(6\,^4S_{3/2})$ by time-resolved resonance fluorescence, following earlier investigations in this research group demonstrating the use of the $\lambda = 306.8$ nm fluorescence transition $Bi(7\,^4P_{1/2})$ $\rightarrow Bi(6\,^4S_{3/2}) + h\nu$ as a kinetic tool for monitoring ground state bismuth atoms as a function of time [13]. In this paper we describe detailed kinetic studies of the overall processes $Bi(6\,^4S_{3/2}) + O_2 + M$ and $Bi(6\,^4S_{3/2}) + NO + M$ (M $\equiv$ He, N_2 and CF_4) using this method [12]. These reactions have not been investigated hitherto by the resonance fluorescence technique. Detailed investigations show both classes of reaction to be third order in the pressure ranges studied here, and absolute third-order rate constants are reported and compared with previous data, where possible, and with other analogous third-order reactions of $Sb(5\,^4S_{3/2})$, $Pb(6\,^3P_0)$ and $Sn(5\,^3P_0)$.

2. Experimental details

The details of the experimental arrangement have been given in the preceding paper [12]. Briefly, $Bi(6\,^4S_{3/2})$ was generated by the pulsed irradiation of $Bi(CH_3)_3$ from a high pressure discharge through krypton ($p_{Kr} = 1$ atm; $E = 320$ J) and monitored in the "single-shot" mode with time-resolved resonance fluorescence at $\lambda = 306.8$ nm ($Bi(7\,^4P_{1/2}) \rightarrow Bi(6\,^4S_{3/2}) + h\nu$) following optical excitation using a microwave-powered cavity constructed after the design of Beenakker [14 - 16]. The resonance fluorescence signals at $\lambda = 306.8$ nm, representing the decay of $Bi(6\,^4S_{3/2})$, were optically isolated by means of an interference filter, monitored photoelectrically, where the signals were amplified without distortion, recorded and digitized in a transient recorder and subsequently punched onto paper tape in ASCII code for input into the University of Cambridge computer (IBM 3081). All materials (helium, krypton, N_2, O_2, NO, CF_4, BiI_3 and $Bi(CH_3)_3$) were prepared as described in previous publications [6, 8, 12, 13, 17].

3. Results and discussion

3.1. Bi + NO + M

Figure 1(a) gives an example of the digitized time variation of the fluorescence intensity I_F at $\lambda = 306.8$ nm $(\text{Bi}(7\,^4\text{P}_{1/2}) \rightarrow \text{Bi}(6\,^4\text{S}_{3/2}) + h\nu)$ following the pulsed irradiation of $\text{Bi}(\text{CH}_3)_3$ in the presence of excess N_2, and Fig. 1(b) shows the effect on the decay of $\text{Bi}(6\,^4\text{S}_{3/2})$ by the addition of NO. The curves in Fig. 1 represent numerical fittings (IBM CalComp plotter) to the form

$$I_F = \theta_1 + \theta_2 \exp(-k't) \tag{1}$$

where

$$\theta_2 \exp(-k't) = \frac{\phi[\text{Bi}(6\,^4\text{S}_{3/2})]_{t=0} \exp(-k't)}{1 + \Sigma k_Q[Q]/A_{nm}} \tag{2}$$

(a)

(b)

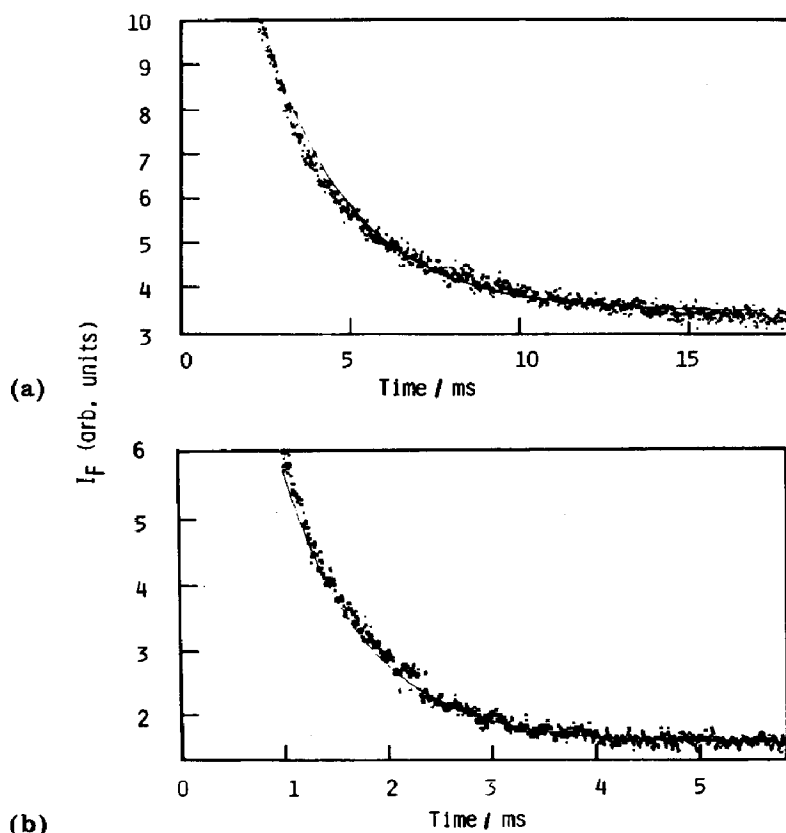Fig. 1. Digitized time variation in the light intensity I_F at $\lambda = 306.8$ nm $(\text{Bi}(7\,^4\text{P}_{1/2}) \rightarrow \text{Bi}(6\,^4\text{S}_{3/2}))$ indicating the decay of resonance fluorescence due to ground state bismuth atoms for (a) [NO] = 0 and (b) [NO] = 4.8×10^{16} molecules cm^{-3} ([$\text{Bi}(\text{CH}_3)_3$] = 3.2×10^{14} molecules cm^{-3}; [N_2] = 1.6×10^{18} molecules cm^{-3}; $E = 320$ J): ×, data points; ———, computerized curve fitting to the form $I_F = \theta_1 + \theta_2 \exp(-k't)$.

as described previously [12]. We have stressed [12] that the fitting by computer initially employed Powell's "Lamfit" procedure [18] to the data to determine θ_1 and the subsequent regression procedure of $I_F - \theta_1$ on t in napierian logarithmic form to determine k', the first-order decay coefficient of $Bi(6\,^4S_{3/2})$, the object of kinetic interest. Examples of this procedure for the data of Fig. 1 are given in Fig. 2 and constitute the standard first-order kinetic plots for the decay of atomic bismuth. The scatter in the data in the form of Fig. 2 clearly increases at long time when $I_F - \theta_1$ becomes small but the error in the value of k' is not large on this account (typically 1% - 3%) as a result of the large number of points (1024) available in the transient recorder. Figure 2 is presented here simply to give examples of the form of the first-order kinetic plots in relation to the raw data. In general terms, all kinetic data in this paper are analysed numerically in the form of a regression of $\ln(I_F - \theta_1)$ on t. Examples of numerical fittings of the raw data are given
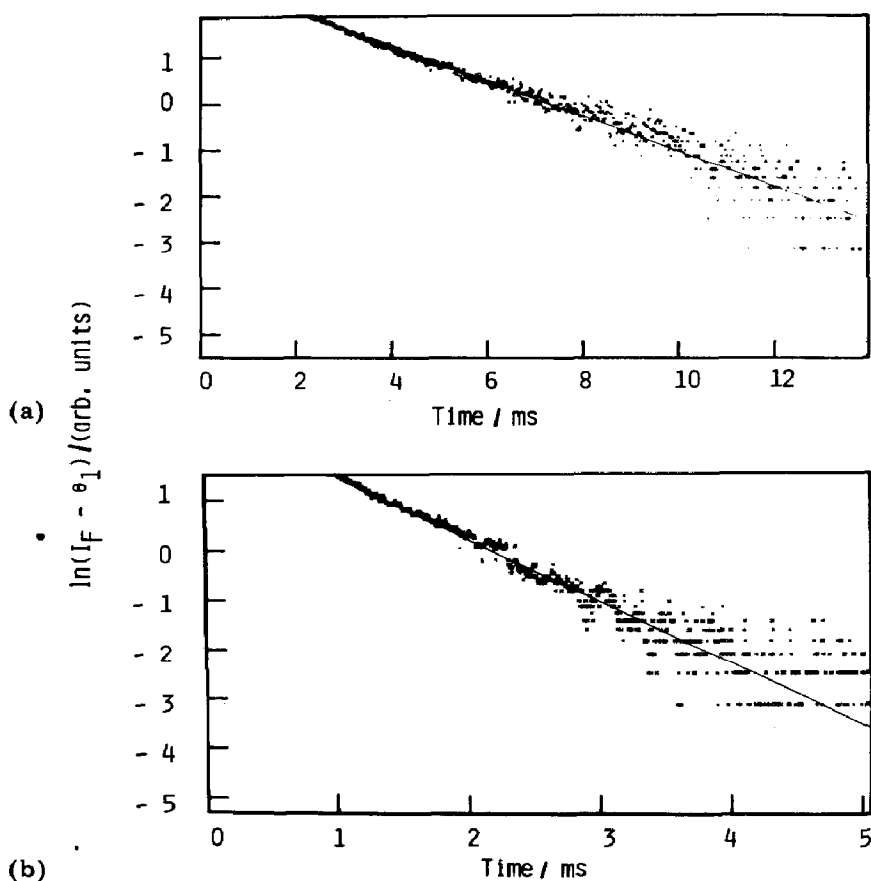

Fig. 2. Computerized output of the digitized first-order kinetic plots derived from time-resolved atomic resonance fluorescence measurements at $\lambda = 306.8$ nm $(Bi(7\,^4P_{1/2}) \rightarrow Bi(6\,^4S_{3/2}))$ due to the kinetic removal of ground state bismuth atoms for (a) $[NO] = 0$ and (b) $[NO] = 4.8 \times 10^{16}$ molecules cm^{-3} $([Bi(CH_3)_3] = 3.2 \times 10^{14}$ molecules cm^{-3}; $[N_2] = 1.6 \times 10^{18}$ molecules cm^{-3}; $E = 320$ J): $\times$, data points; ———, computerized fitting to the form $\ln(I_F - \theta_1)$ vs. t.

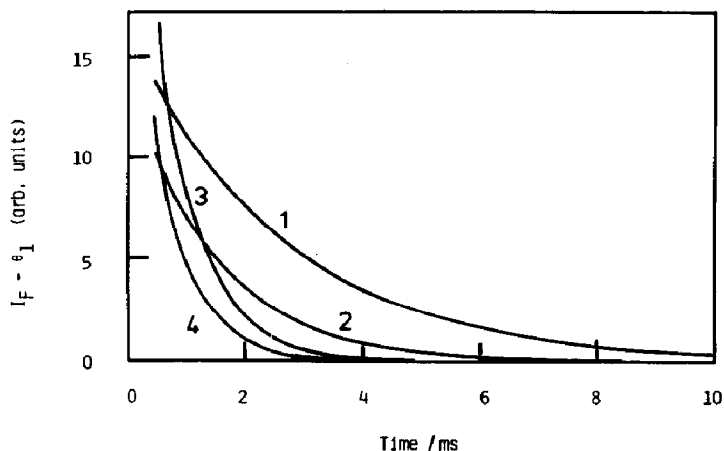Fig. 3. Computerized curve fitting of the experimental intensity profiles for the decay of $Bi(6\,^4S_{3/2})$ obtained by time-resolved atomic resonance fluorescence at $\lambda = 306.8$ nm $(Bi(7\,^4P_{1/2}) \rightarrow Bi(6\,^4S_{3/2}))$ $((I_F - \theta_1)$ vs. $t)$ in the presence of various concentrations of NO ($[Bi(CH_3)_3] = 3.1 \times 10^{14}$ molecules cm^{-3}; $[N_2] = 1.6 \times 10^{18}$ molecules cm^{-3}; $E = 320$ J): curve 1, 0.0; curve 2, 2.4×10^{16} molecules cm^{-3}; curve 3, 4.4×10^{16} molecules cm^{-3}; curve 4, 5.5×10^{16} molecules cm^{-3}.

in Fig. 3 in the form of $(I_F - \theta_1)$ *versus* t for various concentrations of NO. Thus, the overall analyses yield values of θ_1, θ_2 and k'. We have given examples in the previous paper [12] of the use of θ_2 for fluorescence quenching measurements through the application of eqn. (2), including the determination of cross sections for the collisional removal of $Bi(7\,^4P_{1/2})$ by reactant gases investigated in this paper. Here, only the values of k' are considered.

The analyses of k' in these experiments take particular account of the correction due to diffusional loss of $Bi(6\,^4S_{3/2})$, which is especially significant in time-resolved resonance fluorescence measurements where the total pressure is varied. As we indicated [12], this arises because the geometry of the effective reaction volume, due to the overlap of the cones of light from the pulsed initiation source, the resonance source and the light collection of the detection optics, is a small fraction of the total physical size of the reaction vessel. Whilst the actual effective dimensions of this small volume are not normally quantified, the small geometrical parameters of this volume have a large effect on the first-order contribution to k' through the "long-time solution" of the diffusion equation [19, 20] resulting from the effect of the reciprocal of the square of the dimensions. This is clearly manifest in the data presented here (Fig. 4 and subsequent data).

Following the earlier studies [12], the first-order decay coefficient k' of $Bi(6\,^4S_{3/2})$ can be expressed in the form

$$k' = K + \frac{\beta}{p_M} + k_3[\text{NO}][\text{M}] \qquad (3)$$

for this particular reaction. M is the third body, k_3 is the appropriate absolute third-order rate constant for the overall removal of $Bi + NO + M$ and β/p_M is the first-order contribution to the loss of $Bi(6\,^4S_{3/2})$ by diffusion. In
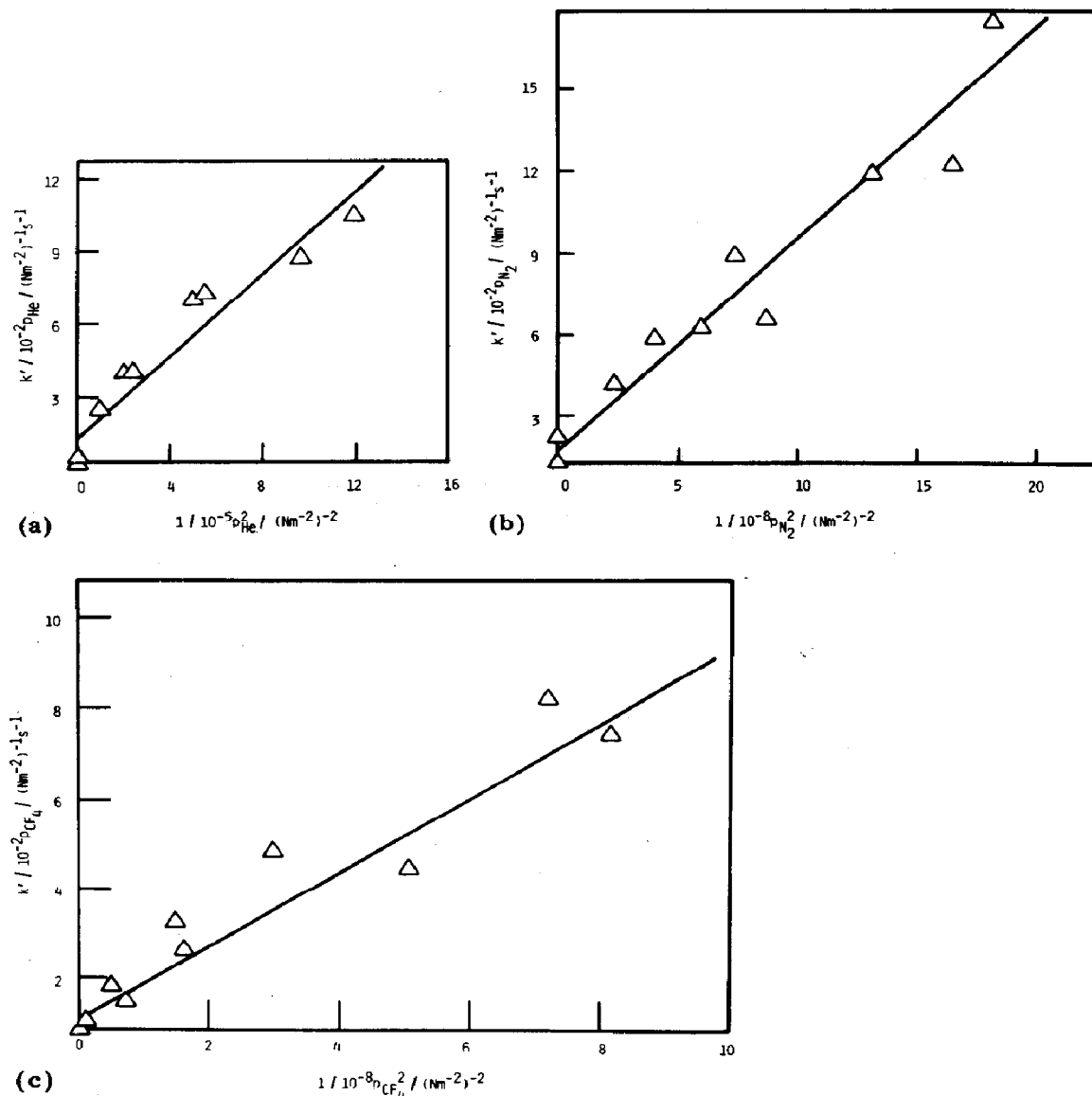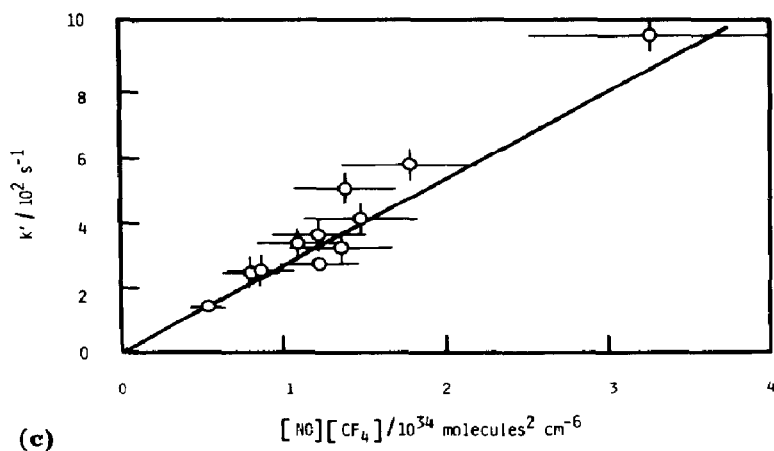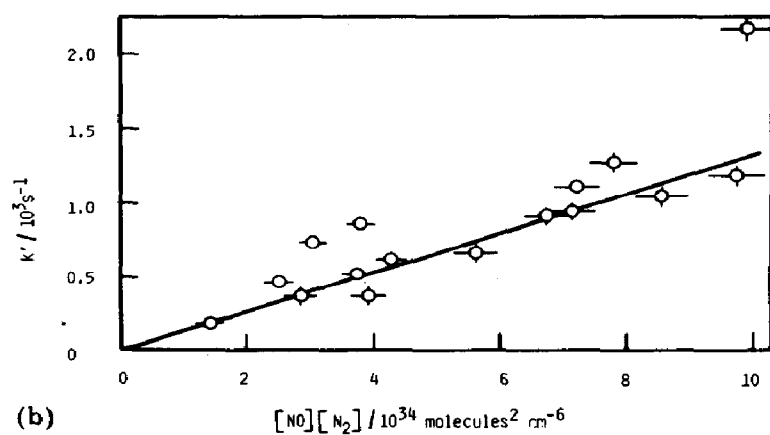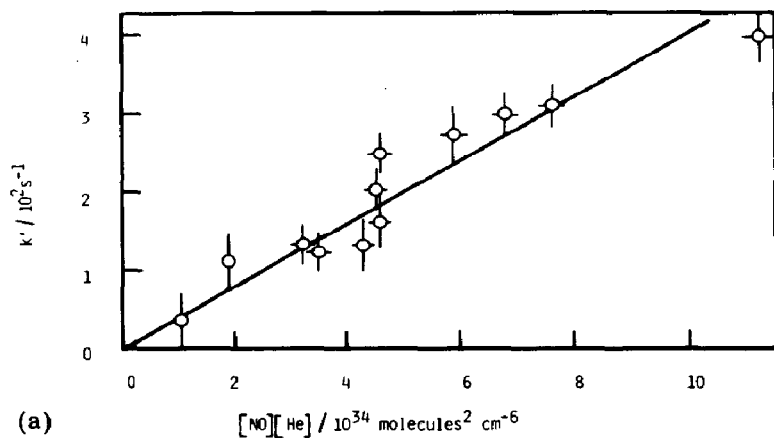
Fig. 4. Variation in the pseudo-first-order rate coefficient k' for the decay of $Bi(6^4S_{3/2})$ in the presence of NO and M (k'/p_M vs. $1/p_M^2$) indicating the effects of both third-order kinetics and diffusion ($[Bi(CH_3)_3] = 2.3 \times 10^{14}$ molecules cm^{-3}; $[NO] \approx 2.1 \times 10^{16}$ molecules cm^{-3}; $E = 320$ J): (a) M $\equiv$ He; (b) M $\equiv$ N_2; (c) M $\equiv$ CF_4.

the present studies the term K, representing the loss of atomic bismuth by reaction with $Bi(CH_3)_3$ or photolysis fragments, is negligible (about 50 s^{-1} or less) and difficult to detect. When such corrections are necessary, these would be of the order of 5%. Thus, eqn. (3) is cast in the form

$$\frac{k'}{p_M} = \alpha + \frac{\beta}{p_M^2} \tag{4}$$

Fig. 5. Variation in the pseudo-first-order rate coefficient k' (diffusion corrected and normalized) for the decay of $Bi(6\,^4S_{3/2})$ in the presence of NO and M: (a) M $\equiv$ He; (b) M $\equiv$ N$_2$; (c) M $\equiv$ CF$_4$.

Figure 4 shows the data for the removal of $Bi(6\,^4S_{3/2})$ in the form of eqn. (4) for a fixed concentration of NO with $M \equiv He$, N_2 and CF_4. The intercepts of these plots yield $k_3[NO]$ for the various third bodies M. Figure 5 shows the plots of k' (diffusion corrected) *versus* $[NO][M]$ for $M \equiv He$, N_2 and CF_4, the slopes of which yield the absolute third-order rate constants k_3 (cm^6 molecule^{-2} s^{-1}) (300 K; errors, 2σ): $k_3(Bi + NO + He) = (3.9 \pm 0.4) \times 10^{-33}$; $k_3(Bi + NO + N_2) = (1.3 \pm 0.2) \times 10^{-32}$; $k_3(Bi + NO + CF_4) = (2.7 \pm 0.8) \times 10^{-32}$.

3.2. Bi + O₂ + M

Analyses of the digitized forms of I_F ($\lambda = 306.8$ nm) *versus* t were carried out for measurements on the decay of $Bi(6\,^4S_{3/2})$ in the presence of O_2 and M. An analogous set of examples to those given in Fig. 3 for the decay of $Bi(6\,^4S_{3/2})$ in the presence of NO (fixed $[N_2]$) are given in Fig. 6 for the decay of atomic bismuth in the presence of O_2 (($I_F - \theta_1$) *versus* t; fixed $[N_2]$). Figure 7 gives an example of plots of the type given in Fig. 4, in this case, for the diffusion-corrected removal of $Bi(6\,^4S_{3/2})$ in the presence of a fixed $[O_2]$ and N_2 according to the analogous eqns. (3) and (4), here for $Bi + O_2 + M$. Finally, Fig. 8 shows the analogous plots of those given in Fig. 5 for $Bi + NO + M$, namely k' (diffusion corrected) *versus* $[O_2][M]$ for $M \equiv He$, N_2 and CF_4. The slopes of these plots (Fig. 8) thus yield the absolute third-order rate constants for the removal of $Bi(6\,^4S_{3/2})$ by O_2 plus He, N_2 or CF_4. The data for N_2 demonstrate some curvature at high pressure and the slope of essentially the first half of Fig. 8(b) was used to determine the third-order rate constant. The following results were obtained for k_3 (cm^6 molecule^{-2} s^{-1}) (300 K; errors, 2σ): $k_3(Bi + O_2 + He) = (3.3 \pm 0.3) \times 10^{-32}$; $k_3(Bi + O_2 + N_2) = (8.9 \pm 0.9) \times 10^{-32}$; $k_3(Bi + O_2 + CF_4) = (1.3 \pm 0.2) \times 10^{-31}$.
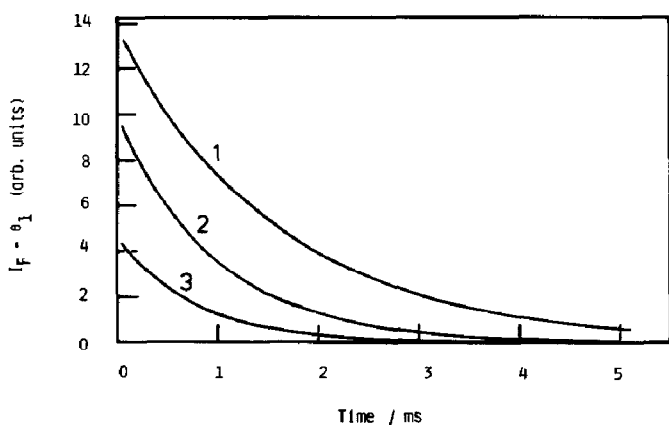

Fig. 6. Computerized curve fitting of the experimental intensity profiles for the decay of $Bi(6\,^4S_{3/2})$ obtained by time-resolved atomic resonance fluorescence at $\lambda = 306.8$ nm ($Bi(7\,^4P_{1/2}) \rightarrow Bi(6\,^4S_{3/2})$) (($I_F - \theta_1$) *vs.* t) in the presence of various concentrations of O_2 ($[Bi(CH_3)_3] = 7.2 \times 10^{14}$ molecules cm^{-3}; $[N_2] = 1.1 \times 10^{18}$ molecules cm^{-3}; $E = 320$ J): curve 1, 0.55×10^{16} molecules cm^{-3}; curve 2, 1.0×10^{16} molecules cm^{-3}; curve 3, 1.8×10^{16} molecules cm^{-3}.
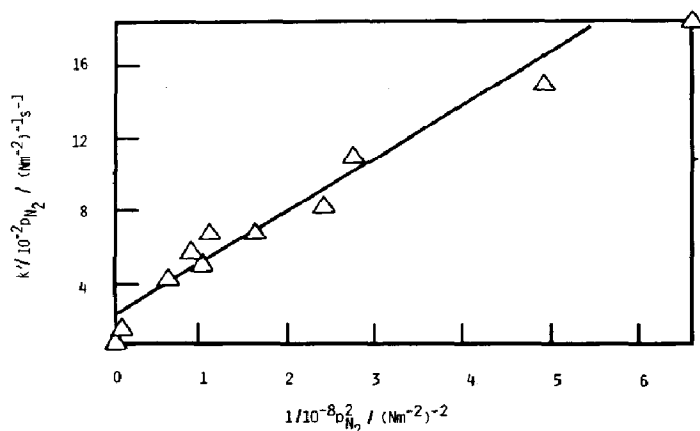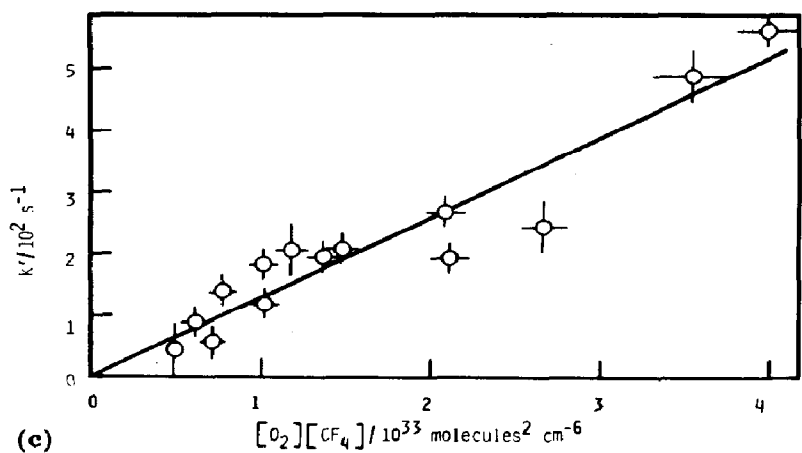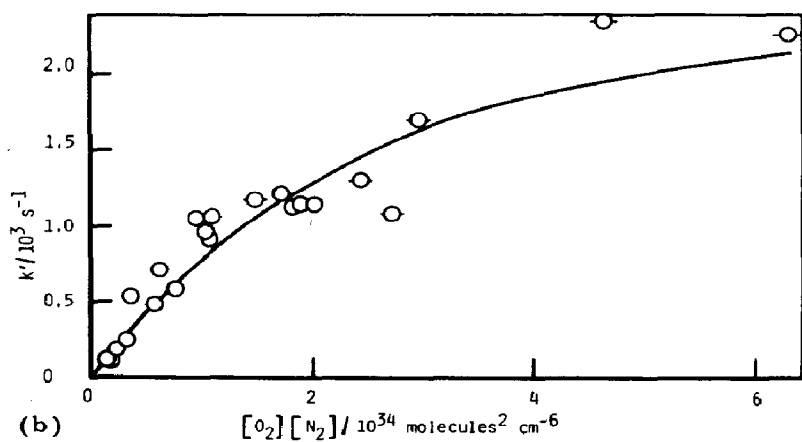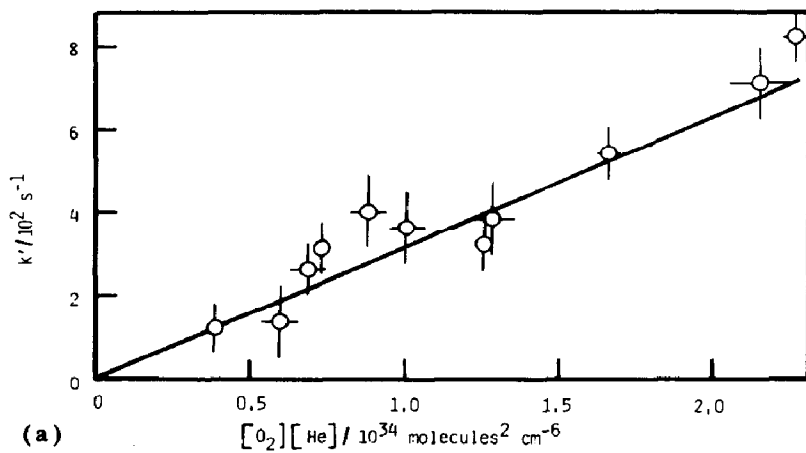
Fig. 7. Variation in the pseudo-first-order rate coefficient k' for the decay of $Bi(6\,^4S_{3/2})$ in the presence of O_2 and N_2 (k'/p_{N_2} vs. $1/p_{N_2}^2$) indicating the effects of both third-order kinetics and diffusion ($[Bi(CH_3)_3] = 2.6 \times 10^{14}$ molecules cm^{-3}; $[O_2] = 1.1 \times 10^{16}$ molecules cm^{-3}; $E = 320$ J).

3.3. Discussion

The time-resolved resonance absorption measurements that have been reported for the removal of $Bi(6\,^4S_{3/2})$ in the presence of O_2 indicated complex kinetics for the relatively high concentrations of this molecule and only an estimate of $k_3(Bi + O_2 + He) \approx 3 \times 10^{-32}$ cm^6 molecule^{-2} s^{-1} (300 K) was reported [8]. This was derived from $[O_2] \lesssim 4 \times 10^{16}$ molecules cm^{-3} where the removal of $Bi(6\,^4S_{3/2})$ could be sensibly described by overall third-order kinetics. The present measurements are restricted to this region (e.g. Fig. 6) to avoid the effects of the competing processes that evidently become significant at a high concentration of O_2. The present results are of comparable magnitude with those reported for $Pb(6\,^3P_0) + O_2 + M$ (Table 1) and somewhat lower than those measured for $Sb(5\,^4S_{3/2}) + O_2 + M$ [7] (Table 1). The data for $k_3(Sb + O_2 + He)$ derived from time-resolved atomic resonance fluorescence monitoring [21] were obtained from measurements carried out at a single pressure ($p_{He} = 2.5$ kN m^{-2}) assuming third-order kinetics. The trend in the rate data for $Bi + O_2 + M$ for the different third bodies is clearly consistent with general trends for such third-order processes as are the absolute magnitudes of the rate constants, which indicate a mean lifetime of the initially energized BiO_2^* of magnitude about 10^{-12} s.

By contrast with the time-resolved resonance absorption measurements on $Bi(6\,^4S_{3/2})$ which describe second-order kinetics for the removal of the atom in the presence of NO [8], the resonance fluorescence measurements here clearly indicate third-order kinetics (Table 2). Husain and Slater [8] reported a second-order rate constant for the removal of $Bi(6\,^4S_{3/2})$ by NO in the presence of He, N_2 and SF_6, at total pressures of 5.3 kN m^{-2}, of $(5.6 \pm 0.1) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (300 K; 1σ). This would correspond to a third-order rate constant of 4.4×10^{-32} cm^6 molecule^{-2} s^{-1}, which is

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(a)

(b)

(c)

Fig. 8. Variation in the pseudo-first-order rate coefficient k' (diffusion corrected and normalized) for the decay of $Bi(6\,^4S_{3/2})$ in the presence of O_2 and M: (a) M $\equiv$ He; (b) M $\equiv$ N_2; (c) M $\equiv$ CF_4.

TABLE 1

Absolute third-order rate constants $k_3(X + O_2 + M)$ $(cm^6$ molecule^{-2} s$^{-1})$ $(T = 300$ K) derived from time-resolved atomic spectroscopic monitoring following pulsed irradiation

M	$k_3(X + O_2 + M)$ $(cm^6$ molecule^{-2} s$^{-1})$ for the following species X		
	$Bi(6\,^4S_{3/2})$	$Sb(5\,^4S_{3/2})$	$Pb(6\,^3P_0)$
He	$(3.3 \pm 0.3) \times 10^{-32}$ [a,b] $\approx 3 \times 10^{-32}$ [8][c]	$(2.2 \pm 0.2) \times 10^{-31}$ [7][c] $(1.8 \pm 0.2) \times 10^{-31}$ [21][b]	$(1.4 \pm 0.5) \times 10^{-32}$ [1][c]
N_2	$(8.9 \pm 0.9) \times 10^{-32}$ [a,b]	$(3.2 \pm 0.3) \times 10^{-31}$ [7][c]	$(3.2 \pm 0.5) \times 10^{-32}$ [1][c]
CF_4	$(1.3 \pm 0.2) \times 10^{-31}$ [a,b]	$((3.6 \pm 0.4) \times 10^{-31}$ [7][c] M $\equiv$ SF$_6$)	$(3.9 \pm 0.3) \times 10^{-32}$ [1][c]

[a] This work.
[b] Time-resolved atomic resonance fluorescence.
[c] Time-resolved atomic resonance absorption.

TABLE 2

Absolute third-order rate constants $k_3(X + NO + M)$ $(cm^6$ molecule^{-2} s$^{-1})$ (300 K) derived from time-resolved atomic spectroscopic monitoring following pulsed irradiation

M	$k_3(X + NO + M)$ $(cm^6$ molecule^{-2} s$^{-1})$ for the following species X		
	$Bi(6\,^4S_{3/2})$	$Pb(6\,^3P_0)$	$Sn(5\,^3P_0)$
He	$(3.9 \pm 0.4) \times 10^{-33}$ [a,b]	2×10^{-30} [1][c] 2.6×10^{-30} [1][c]	$(5.1 \pm 0.4) \times 10^{-30}$ [6][c]
N_2	$(1.3 \pm 0.2) \times 10^{-32}$ [a,b]	$(1.2 \pm 0.2) \times 10^{-30}$ [1][c]	
CF_4	$(2.7 \pm 0.8) \times 10^{-32}$ [a,b]	$(3.1 \pm 1.1) \times 10^{-30}$ [1][c]	

[a] This work.
[b] Time-resolved atomic resonance fluorescence.
[c] Time-resolved atomic resonance absorption.

comparable with data indicated in Table 2. Some preliminary unpublished resonance fluorescence measurements on the removal of $Bi(6\,^4S_{3/2})$ by NO carried out by the same researchers [22] yielded a second-order rate constant of $(3.0 \pm 0.3) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (300 K; 1σ) which would reduce the value of a calculated third-order rate constant correspondingly. The third-order rate data for Bi + NO + M are significantly slower than those reported for $Pb(6\,^3P_0)$ + NO + M [1] (Table 2), indicating a lifetime of the initially generated BiNO* of magnitude about 2×10^{-13} s, somewhat shorter than that estimated for BiO$_2$*.

References

1 P. J. Cross and D. Husain, *J. Photochem.*, *7* (1977) 157.
2 D. Husain and J. G. F. Littler, *J. Photochem.*, *2* (1974) 247.
3 D. Husain and J. G. F. Littler, *Combust. Flame*, *22* (1974) 295.
4 K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. IV, *Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1979.
5 P. D. Foo, J. R. Wiesenfeld and D. Husain, *Chem. Phys. Lett.*, *32* (1975) 443.
6 M. A. Chowdhury and D. Husain, *J. Chem. Soc., Faraday Trans. II*, *74* (1978) 1065.
7 D. Husain and N. K. H. Slater, *J. Photochem.*, *7* (1977) 59.
8 D. Husain and N. K. H. Slater, *J. Photochem.*, *6* (1977) 325.
9 S. D. Kramer, B. E. Lehman, G. S. Hurst, M. G. Payne and J. P. Young, *J. Chem. Phys.*, *76* (1982) 3614.
10 D. Husain and J. M. C. Plane, *J. Chem. Soc., Faraday Trans. II*, *78* (1982) 163.
11 D. Husain and J. M. C. Plane, *J. Chem. Soc., Faraday Trans. II*, *78* (1982) 1175.
12 C. F. Bell and D. Husain, *J. Photochem.*, *24* (1984) 207.
13 D. Husain, L. Krause and N. K. H. Slater, *J. Chem. Soc., Faraday Trans. II*, *73* (1977) 1678.
14 C. I. M. Beenakker, *Spectrochim. Acta, Part B*, *31* (1976) 483.
15 C. I. M. Beenakker, *Spectrochim. Acta, Part B*, *32* (1977) 173.
16 C. I. M. Beenakker and P. W. J. Boumans, *Spectrochim. Acta, Part B*, *33* (1978) 53.
17 D. Husain and J. Schifino, *J. Chem. Soc., Faraday Trans. II*, *78* (1982) 2083.
18 M. J. D. Powell, personal communication, 1979, cited in D. Husain and N. K. H. Slater, *J. Chem. Soc., Faraday Trans. II*, *76* (1980) 606.
19 M. W. Zemansky, *Phys. Rev.*, *34* (1929) 213.
20 A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms*, Cambridge University Press, London, 1934.
21 D. Husain, L. Krause and N. K. H. Slater, *J. Chem. Soc., Faraday Trans. II*, *73* (1977) 1706.
22 D. Husain and N. K. H. Slater, unpublished results, 1977.