

A KINETIC STUDY OF THE THIRD ORDER REACTIONS OF ATOMIC LEAD, $\text{Pb}(6^3\text{P}_0) + \text{C}_2\text{H}_2 + \text{M}$ AND $\text{Pb}(6^3\text{P}_0) + \text{C}_2\text{H}_4 + \text{M}$

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Summary

We describe a kinetic study of the overall third order processes $\text{Pb} + \text{C}_2\text{H}_2 + \text{M}$ (reaction (1)) and $\text{Pb} + \text{C}_2\text{H}_4 + \text{M}$ (reaction (2)) by resonance line absorption measurements on the $\text{Pb}(6^3\text{P}_0)$ ground state. These atoms were generated by pulsed irradiation and monitored photoelectrically in absorption in the single-shot time-resolved mode at $\lambda = 283.3 \text{ nm}$ ($\text{Pb}(7s(^3\text{P}_1^o) \leftarrow \text{Pb}(6p^2(^3\text{P}_0)))$). Absolute third order rate constants (at 300 K in units of $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$) are reported for the following third bodies M: reaction (1), $10^{33}k_1$ — He (1.3 ± 0.2), N_2 (2.6 ± 0.3), CO_2 (3.9 ± 0.3), CH_4 (5.3 ± 0.6) and SF_6 (4.5 ± 0.5); reaction (2), $10^{33}k_2$ — He (1.2 ± 0.1), N_2 (4.2 ± 0.3), CO_2 (5.0 ± 0.3), CH_4 (3.7 ± 0.6) and SF_6 (5.6 ± 0.3). These data are compared, where possible, with data for analogous reactions of $\text{Sn}(5^3\text{P}_0)$, $\text{Sb}(5^4\text{S}_{3/2})$ and $\text{Bi}(6^4\text{S}_{3/2})$, and also with rate data for $\text{Pb} + \text{Pb} + \text{M}$ and $\text{Pb} + \text{O}_2 + \text{M}$.

1. Introduction

Kinetic studies of lead atoms have been carried out on all the states arising from the overall $6p^2$ ground state configuration ($6^3\text{P}_{0,1,2}$, 6^1D_2 , 6^1S_0) by resonance line absorption following pulsed irradiation [1 - 14]. Studies of the $^3\text{P}_0$ ground state atom by this method include systematic investigation of atom-molecule recombination processes of the type $\text{Pb} + \text{O}_2 + \text{M}$ and $\text{Pb} + \text{NO} + \text{M}$ for a wide range of third bodies M [3]. By contrast, experimental measurement of the rates of atomic recombination $\text{Pb} + \text{Pb} + \text{M}$ was not found to be amenable to the resonance line absorption method [5], principally on account of the difficulty in extracting at high optical densities a kinetic component, second order in atomic concentration, from the more dominant first order component. Hence the rates of such processes were calculated by the phase space variational method of Keck [5, 15, 16]. An interesting class of atomic reactions within a similar context is that of the overall third order removal of the ground state

Pb(6^3P_0) atom by the unsaturated molecules C_2H_2 and C_2H_4 . A limited number of analogous studies have been described for Sn(5^3P_0) [17], and also for Sb($5^4S_{3/2}$) [18] and Bi($6^4S_{3/2}$) [19]. In this paper we describe measurements of the absolute third order rate constants for Pb + C_2H_2 + M and Pb + C_2H_4 + M where M is He, N_2 , CO_2 , CH_4 and SF_6 . The resulting rate data are compared, where possible, with the analogous data for tin, antimony and bismuth atoms [17, 19], and with the data reported previously for Pb + O_2 + M [3] and Pb + Pb + M [5].

2. Experimental

The experimental arrangement was similar to that employed in previous kinetic studies on Pb(6^3P_0) [3 - 6], with minor modifications principally to the reaction vessel and the photolysis lamp assembly. In this case a conventional reaction vessel and photolysis lamp, separated from each other by an air gap and optically coupled by means of aluminium foil, were employed. Pb(6^3P_0) was then generated by the pulsed irradiation of lead tetraethyl (PbEt₄) in the presence of excess buffer gas to ensure no significant temperature rise on photolysis. Low flash energies, typically $E = 65$ J ($C = 2.5 \mu F$, $V = 7.2$ kV), were employed in order to minimize the photochemical production of any optically metastable states, particularly the low lying spin-orbit states Pb(6^3P_1) ($E = 0.97$ eV) and Pb(6^3P_2) ($E = 1.32$ eV) [20]. Furthermore, kinetic experiments were carried out at pressures of added gases, including the unsaturated hydrocarbons C_2H_2 and C_2H_4 and the third bodies M and in long-time domains relative to the initiation pulse, which were sufficient to ensure the complete relaxation of any optically metastable states that were generated photochemically to the 3P_0 ground state [7 - 14]. The transient atoms were then monitored photoelectrically by resonance line absorption at $\lambda = 283.3$ nm (Pb($7s(^3P_1^o)$) \leftarrow Pb($6p^2(^3P_0)$)), $gA = 1.8 \times 10^8$ s⁻¹ [21]). The optical system described elsewhere (Seya-Namioka grating monochromator, E.M.I. photomultiplier tube 9783B) [4, 5, 22 - 24] was employed for isolation and detection of the atomic line. The resonance absorption signals were then amplified [25], transferred to a transient recorder (Data Laboratories, DL905) employed in the A/B mode [3, 4], digitized, stored and transferred onto paper tape (Data Dynamics Punch 1133) in ASCII code for direct input into the University of Cambridge IBM 370 computer. The raw data were subjected to the standard smoothing procedure of Savitsky and Golay [26].

The resonance absorption signals were analysed according to the modified Beer-Lambert law [27]:

$$I_{tr} = I_0 \exp\{-\epsilon(cl)^\gamma\} \quad (I)$$

This law has been reinvestigated recently in detail for the $\lambda = 283.3$ nm transition both in terms of the standard empirical calibration procedure [27] and in terms of the experimental determination of the curve of growth [28]

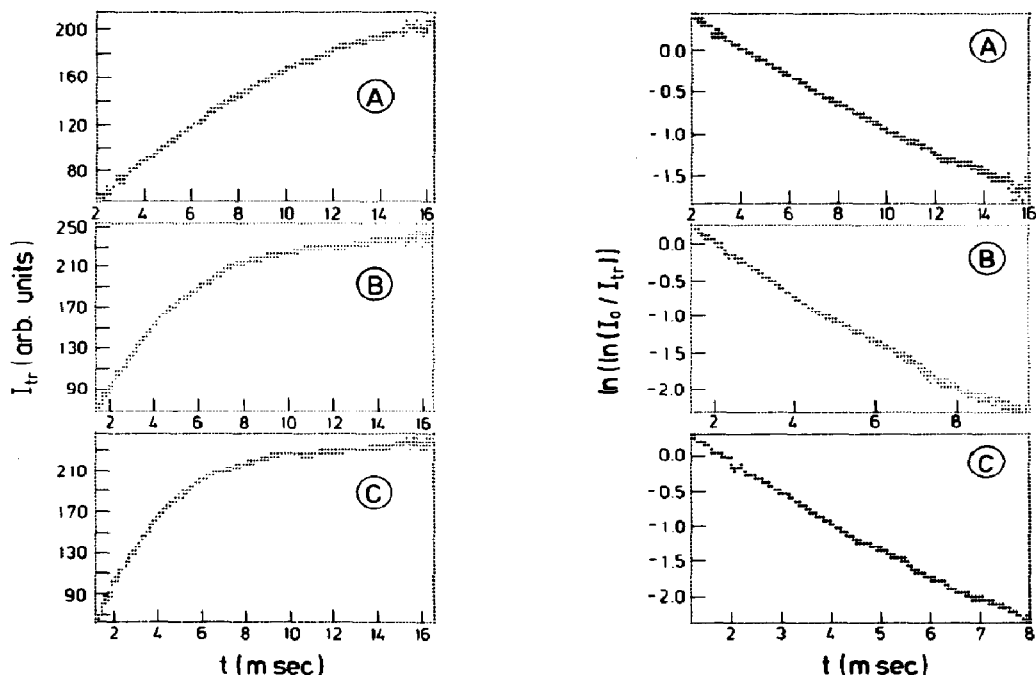


Fig. 1. Digitized time variation of the transmitted light intensity at $\lambda = 283.3$ nm ($\text{Pb}(7s\ ^3\text{P}_1^o) \rightarrow \text{Pb}(6p\ ^2\ ^3\text{P}_0)$) indicating the decay of resonance absorption by ground state lead atoms: (a) $[\text{PbEt}_4] = 6.6 \times 10^{14}$ molecules cm^{-3} , $[\text{CO}_2] = 5.5 \times 10^{17}$ molecules cm^{-3} , $E = 61$ J; (b) $[\text{PbEt}_4] = 7.4 \times 10^{14}$ molecules cm^{-3} , $[\text{CO}_2] = 1.3 \times 10^{18}$ molecules cm^{-3} , $[\text{C}_2\text{H}_2] = 8.4 \times 10^{16}$ molecules cm^{-3} , $E = 65$ J; (c) $[\text{PbEt}_4] = 6.6 \times 10^{14}$ molecules cm^{-3} , $[\text{CO}_2] = 1.6 \times 10^{18}$ molecules cm^{-3} , $[\text{C}_2\text{H}_4] = 6.9 \times 10^{16}$ molecules cm^{-3} , $E = 61$ J.

Fig. 2. Pseudo first order plots for the decay of $\text{Pb}(6^3\text{P}_0)$ obtained by monitoring the absorption of light at $\lambda = 283.3$ nm ($\text{Pb}(7s\ ^3\text{P}_1^o) \leftarrow \text{Pb}(6p\ ^2\ ^3\text{P}_0)$): (a) $[\text{PbEt}_4] = 6.6 \times 10^{14}$ molecules cm^{-3} , $[\text{CO}_2] = 5.5 \times 10^{17}$ molecules cm^{-3} , $E = 61$ J; (b) $[\text{PbEt}_4] = 7.4 \times 10^{14}$ molecules cm^{-3} , $[\text{CO}_2] = 1.3 \times 10^{18}$ molecules cm^{-3} , $[\text{C}_2\text{H}_2] = 8.4 \times 10^{16}$ molecules cm^{-3} , $E = 65$ J; (c) $[\text{PbEt}_4] = 6.6 \times 10^{14}$ molecules cm^{-3} , $[\text{CO}_2] = 1.6 \times 10^{18}$ molecules cm^{-3} , $[\text{C}_2\text{H}_4] = 6.9 \times 10^{16}$ molecules cm^{-3} , $E = 61$ J.

constructed from resonance line absorption measurements on atomic lead vapour in equilibrium with solid lead [6]. We employ the value $\gamma = 0.41 \pm 0.04$ derived from the empirical calibration [6] as the experimental conditions are closer to those pertaining in this investigation.

2.1. Materials

All materials (PbEt_4 , krypton (for the photoflash lamp)), He, N_2 , CO_2 , CH_4 , SF_6 , C_2H_2 and C_2H_4) were prepared essentially as described in previous publications [3 - 5, 12].

3. Results and discussion

Figure 1 gives examples of the smoothed computerized form of the digitized output of the transmitted light intensity at $\lambda = 283.3$ nm, indicating

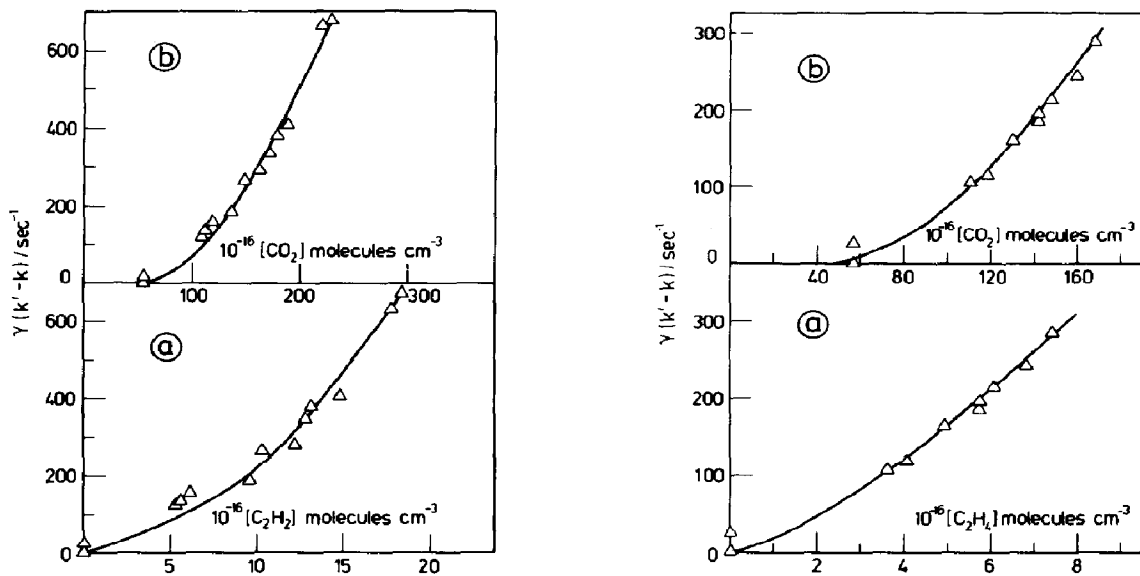


Fig. 3. Variation of the pseudo first-order rate coefficients $\gamma(k' - K)$ for the decay of $\text{Pb}(6^3\text{P}_0)$ in the presence of C_2H_2 and CO_2 : $[\text{PbEt}_4] = 7.4 \times 10^{14} \text{ molecules cm}^{-3}$, $E = 65 \text{ J}$. (a) $\gamma(k' - K)$ vs. $[\text{C}_2\text{H}_2]$ ($[\text{CO}_2]$ also varying). (b) $\gamma(k' - K)$ vs. $[\text{CO}_2]$ ($[\text{C}_2\text{H}_2]$ also varying).

Fig. 4. Variation of the pseudo first-order rate coefficients $\gamma(k' - K)$ for the decay of $\text{Pb}(6^3\text{P}_0)$ in the presence of C_2H_4 and CO_2 : $[\text{PbEt}_4] = 6.6 \times 10^{14} \text{ molecules cm}^{-3}$, $E = 61 \text{ J}$. (a) $\gamma(k' - K)$ vs. $[\text{C}_2\text{H}_4]$ ($[\text{CO}_2]$ also varying). (b) $\gamma(k' - K)$ vs. $[\text{CO}_2]$ ($[\text{C}_2\text{H}_4]$ also varying).

the decay of resonance absorption by $\text{Pb}(6^3\text{P}_0)$ in the presence of CO_2 and with added C_2H_2 and C_2H_4 . Figure 2 shows the computerized first order plots constructed from the data of Fig. 1. The slopes of plots of the type shown in Fig. 2 are given by $-\gamma k'$ where k' is the overall first order coefficient for the decay of $\text{Pb}(6^3\text{P}_0)$ in a given experiment, following eqn. (I). k' can readily be calculated using the value of γ given above. For the case of $\text{CO}_2 + \text{C}_2\text{H}_2$, for example, a series of experiments was carried out in which both C_2H_2 and CO_2 were varied simultaneously. Figure 3 shows that the variation of the first order decay coefficient with either solely $[\text{C}_2\text{H}_2]$ or solely $[\text{CO}_2]$, where the concentrations of both of these reactants in either plot (Fig. 3(a) or 3(b)) are permitted to vary simultaneously, leads, as seen, to curved plots. K represents the first order coefficient for the removal of $\text{Pb}(6^3\text{P}_0)$ by processes other than those involving C_2H_2 or alternatively, for the appropriate experiments, C_2H_4 . Figure 4 shows the analogous plots for experiments carried out with CO_2 and C_2H_4 where, again, both these reactants are permitted to vary simultaneously. For kinetics describing the removal of $\text{Pb}(6^3\text{P}_0)$, which are overall third order, the first order decay coefficient is described by the equation

$$k' = K + k_M[\text{C}_2\text{H}_2 \text{ or } \text{C}_2\text{H}_4] [\text{M}] \quad (\text{II})$$

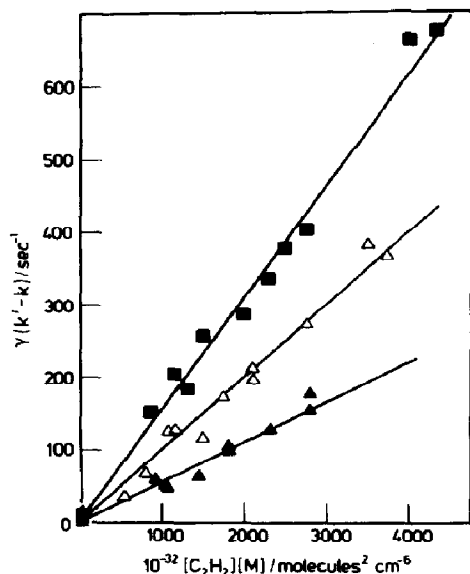


Fig. 5. Variation of the pseudo first order rate coefficient $\gamma(k' - K)$ for the decay of $\text{Pb}(6^3\text{P}_0)$ with $[\text{C}_2\text{H}_2][\text{M}]$: \blacktriangle $\text{M} = \text{He}$, $[\text{PbEt}_4] = 7.0 \times 10^{14}$ molecules cm^{-3} , $E = 61$ J; \triangle $\text{M} = \text{N}_2$, $[\text{PbEt}_4] = 7.5 \times 10^{14}$ molecules cm^{-3} , $E = 53$ J; \blacksquare $\text{M} = \text{CO}_2$, $[\text{PbEt}_4] = 7.4 \times 10^{14}$ molecules cm^{-3} , $E = 65$ J.

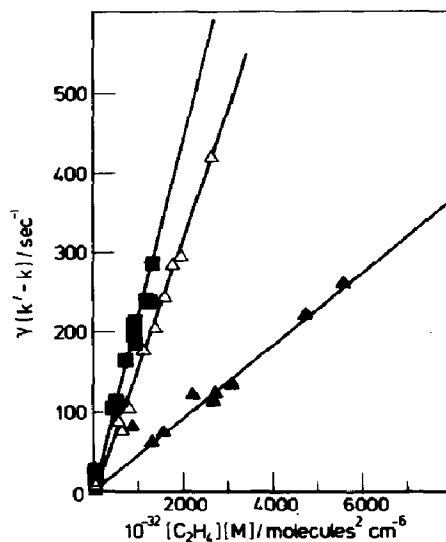


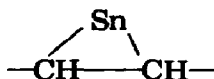
Fig. 6. Variation of the pseudo first order rate coefficient $\gamma(k' - K)$ for the decay of $\text{Pb}(6^3\text{P}_0)$ with $[\text{C}_2\text{H}_4][\text{M}]$: \blacktriangle $\text{M} = \text{He}$, $[\text{PbEt}_4] = 5.7 \times 10^{14}$ molecules cm^{-3} , $E = 61$ J; \triangle $\text{M} = \text{N}_2$, $[\text{PbEt}_4] = 6.0 \times 10^{14}$ molecules cm^{-3} , $E = 53$ J; \blacksquare $\text{M} = \text{CO}_2$, $[\text{PbEt}_4] = 6.6 \times 10^{14}$ molecules cm^{-3} , $E = 65$ J.

Hence a plot of $\gamma(k' - K)$ against $[\text{C}_2\text{H}_2$ or $\text{C}_2\text{H}_4][\text{M}]$ should be linear and of slope γk_M , where k_M is the absolute third order rate constant describing the appropriate overall process:



Figures 5 and 6 show the removal of $\text{Pb}(6^3\text{P}_0)$ by C_2H_2 and C_2H_4 in the presence of the third bodies He, N_2 and CO_2 which is presented graphically in the form of eqn. (II). Thus, for example, the line in Fig. 5 for $\text{M} = \text{CO}_2$ is constructed from the data of Fig. 3. Similar plots are obtained for $\text{M} = \text{SF}_6$ and $\text{M} = \text{CH}_4$ (Figs. 7 and 8). These plots (Figs. 5 - 8) thus yield the overall third order rate constants describing processes (1) and (2). The resulting values are given in Table 1 together with analogous data, where available, for $\text{Sn}(5^3\text{P}_0)$, $\text{Sb}(5^4\text{S}_{3/2})$ and $\text{Bi}(6^4\text{S}_{3/2})$.

Apart from the isolated rate data for $\text{Sn}(5^3\text{P}_0)$ with $\text{M} = \text{He}$ (Table 1), which perhaps reflects the greater facility for ring formation of the type



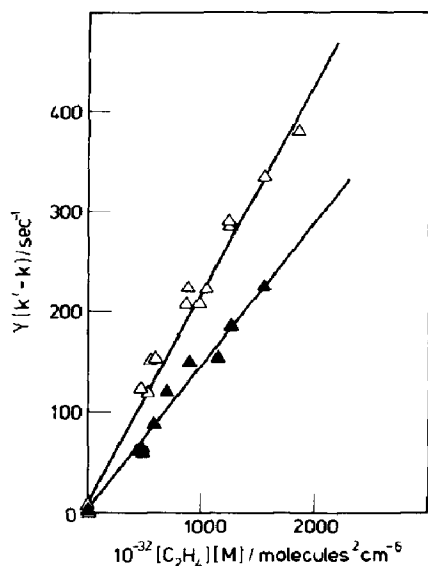


Fig. 7. Variation of the pseudo first order rate coefficient $\gamma(k' - K)$ for the decay of $\text{Pb}(6^3\text{P}_0)$ with $[\text{C}_2\text{H}_4][\text{M}]$: Δ $\text{M} = \text{SF}_6$, $[\text{PbEt}_4] = 6.9 \times 10^{14}$ molecules cm^{-3} , $E = 61$ J; \blacktriangle $\text{M} = \text{CH}_4$, $[\text{PbEt}_4] = 6.2 \times 10^{14}$ molecules cm^{-3} , $E = 61$ J.

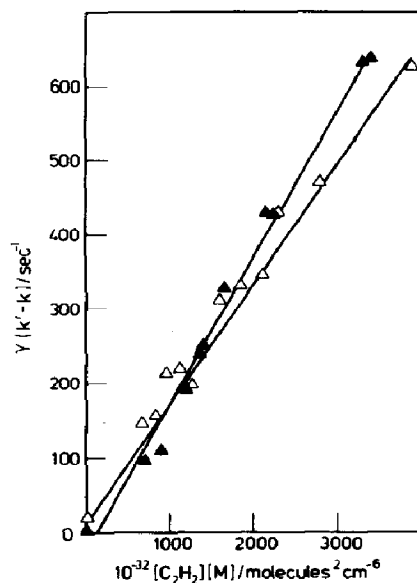


Fig. 8. Variation of the pseudo first order rate coefficient $\gamma(k' - K)$ for the decay of $\text{Pb}(6^3\text{P}_0)$ with $[\text{C}_2\text{H}_2][\text{M}]$: Δ $\text{M} = \text{SF}_6$, $[\text{PbEt}_4] = 7.0 \times 10^{14}$ molecules cm^{-3} , $E = 61$ J; \blacktriangle $\text{M} = \text{CH}_4$, $[\text{PbEt}_4] = 7.2 \times 10^{14}$ molecules cm^{-3} , $E = 61$ J.

the third order rate constants for processes (1) and (2) for $\text{Pb}(6^3\text{P}_0)$ (Table 1) are of the same order of magnitude as those reported previously for $\text{Sb}(5^4\text{S}_{3/2})$ and $\text{Bi}(6^4\text{S}_{3/2})$ [18, 19]. Discussion of the different rates for the different third bodies for processes (1) and (2) clearly involves consideration of small variations in k_M which is no greater than a factor of 5 across the group of third bodies investigated. Hence, we refrain from detailed discussion of the small variation observed for k_M with CH_4 and SF_6 which shows different ordering in efficiencies for C_2H_2 and C_2H_4 (Table 1). Similarly, inspection of the calculated rate constants for $\text{Pb} + \text{Pb} + \text{M}$ [15] shows these to lie in the order $\text{He} < \text{N}_2 < \text{CH}_4 < \text{CO}_2 < \text{SF}_6$ with, again, only a factor of 5 across the group being involved. Similar small variations have been reported for the third order kinetic processes $\text{Pb} + \text{O}_2 + \text{M}$ for He , N_2 , CO_2 and SF_6 [3] although, by contrast, the rate constant for $\text{M} = \text{CH}_4$ is a factor of about 10 greater than that for the other four gases [3]. The detailed mechanism leading to the overall third order kinetics for $\text{Pb} + \text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4 + \text{M}$ presumably involves initial complex formation, probably involving ring insertion, followed by stabilization processes brought about by the third body M .

TABLE 1

Absolute third order rate constants k_M for the collisional removal at 300 K of the atoms (X)Pb(6^3P_0), Sn(5^3P_0), Bi($6^4S_{3/2}$) and Sb($5^4S_{3/2}$) by C₂H₂ and C₂H₄ in the presence of various third bodies M

M	k_M (10^{33} cm ⁶ molecule ⁻¹ s ⁻¹)			
	Pb(6^3P_0)	Sn(5^3P_0)	Bi($6^4S_{3/2}$)	Sb($5^4S_{3/2}$)
X + C ₂ H ₂ + M $\xrightarrow{k_M}$ products				
He	1.3 ± 0.2 ^a	(1.1 ± 0.3) × 10 ³ [17]	1.1 ± 0.1 [18]	9.4 ± 0.1 [19]
N ₂	2.6 ± 0.3 ^a		7.4 ± 0.2 [18]	10.0 ± 1 [19]
CO ₂	3.9 ± 0.3 ^a			
CH ₄	5.3 ± 0.6 ^a			
SF ₆	4.5 ± 0.5 ^a		6.5 ± 0.4 [18]	12 ± 1.4 [19]
X + C ₂ H ₄ + M $\xrightarrow{k_M}$ products				
He	1.2 ± 0.1 ^a	(8.5 ± 2.2) × 10 ² [17]	3.1 ± 0.2 [18]	10 ± 1 [19]
N ₂	4.2 ± 0.3 ^a		8.2 ± 0.7 [18]	11 ± 1 [19]
CO ₂	5.0 ± 0.3 ^a			
CH ₄	3.7 ± 0.6 ^a			
SF ₆	5.6 ± 0.3 ^a		18 ± 1 [18]	11.5 ± 2 [19]

^aThis work.

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