

# KINETIC INVESTIGATION OF THE REACTION OF GROUND STATE LEAD ATOMS $Pb(6^3P_0)$ WITH ALKYL BROMIDES AT ELEVATED TEMPERATURES BY TIME-RESOLVED ATOMIC RESONANCE ABSORPTION SPECTROSCOPY

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## Summary

We present a kinetic investigation of the reactions between ground state lead atoms  $Pb(6p^2(^3P_0))$  and a range of alkyl bromides  $RBr$  in the temperature range 640 - 760 K.  $Pb(6^3P_0)$  was generated by the pulsed irradiation of the  $PbBr_2$  vapour in equilibrium with the solid at the elevated temperatures and monitored by time-resolved atomic resonance absorption spectroscopy at  $\lambda = 283.3$  nm ( $Pb(7^3P_1^o) \leftarrow Pb(6^3P_0)$ ). Absolute second-order rate constants  $k_{RBr}$  for reaction were measured at various temperatures, yielding the following Arrhenius parameters ( $k_{RBr} = A \exp(-E/RT)$ ) (errors  $1\sigma$ ):

RBr	$A$ ( $\times 10^{-10}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$E$ (kJ mol <sup>-1</sup> )
CH <sub>3</sub> Br	$3.0^{+4.9}_{-1.7}$	$63.6 \pm 4.8$
CH <sub>2</sub> Br <sub>2</sub>	$39^{+56}_{-13}$	$59.0 \pm 5.1$
C <sub>2</sub> H <sub>5</sub> Br	$6.6^{+11}_{-3.8}$	$68.3 \pm 6.2$
CH <sub>2</sub> BrCH <sub>2</sub> Br	$46^{+28}_{-4.0}$	$67.2 \pm 11.1$
n-C <sub>3</sub> H <sub>7</sub> Br	$31^{+38}_{-17}$	$74.5 \pm 4.3$

For the molecules 1-bromobutane and 1,3-dibromopropane rate data could be determined only at single temperatures, yielding  $k_{C_4H_9Br} = (2.3 \pm 0.2) \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> ( $T = 639$  K) and  $k_{C_3H_6Br_2} = (3.3 \pm 1.0) \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> ( $T = 740$  K). The activation energies are compared with reaction endothermicities and used to show that the bond energy  $D(PbBr)$  is not more than 2.5 eV. The rate data extrapolated to room temperature indicate that the previously reported values of  $k_{RBr}$  at that temperature are too high and presumably result from the effect of secondary reactions of  $Pb(6^3P_0)$  with photofragments. The diffusion of  $Pb(6^3P_0)$  in helium is studied in detail leading to a value of  $D(Pb(6^3P_0)-He) = 0.48 \pm 0.03$  cm<sup>2</sup> s<sup>-1</sup>, extrapolated to standard temperature and pressure. To the

best of our knowledge, the present measurements constitute the first characterization of absolute rate data for atomic abstraction reactions by lead atoms at elevated temperatures.

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## 1. Introduction

The isolation of fundamental reactions undergone by metal atoms at elevated temperatures in the time domain, leading to absolute rate constants or total cross sections, has received considerable impetus in recent years from various new techniques. The development of the high temperature fast-flow reactor reported by Fontijn and Felder [1] has been particularly useful in the study of reactions of refractory metals. Very recently, a high temperature slow-flow reactor, kinetically equivalent to a static system, in which atoms derived from a heat-pipe flow into the photochemical reactor where transient molecules are generated and monitored spectroscopically, has been reported by Husain and coworkers [2 - 5]. An alternative approach to using a flow of metal vapour is to generate the metal atoms photochemically *in situ* by means of a light pulse and to monitor them in the time domain by atomic resonance absorption spectroscopy. The use of an appropriate time scale will thus permit the isolation of fundamental rate processes. This method is well established for the study of a large range of metal atoms in various electronic states at room temperature [6]. Indeed, it has been employed by Husain and coworkers to determine absolute rate data for the reactions of ground state lead atoms  $\text{Pb}(6p^2(^3P_0))$  with various molecules [7 - 11] including alkyl bromides [12].

The determination of absolute rate data for reactions of metal atoms at elevated temperatures is normally accompanied by complications arising from reactions of the photochemical precursor of the atom or its thermal decomposition, especially if it is a compound such as  $\text{Pb}(\text{C}_2\text{H}_5)_4$  [7 - 12] or  $\text{Pb}(\text{CH}_3)_4$  [13]. The use of metal halides generally overcomes such difficulties and indeed has been the basis of the technique developed by Davidovits and coworkers [14 - 18] to measure total cross sections for reactions of alkali atoms with halogen molecules. This method has been further developed by Husain and coworkers [19 - 22], including the measurement of rate constants for reactions of sodium atoms with substituted alkyl halides, which are analogous to the reactions investigated here [23]. In the present work, the halides of lead, in particular  $\text{PbBr}_2$ , have been used in the study of the reactions of  $\text{Pb}(6^3P_0)$  with various alkyl bromides at elevated temperatures and as a function of temperature. Whilst Husain and Newton have observed  $\text{Pb}(6^3P_0)$  using time-resolved atomic resonance absorption spectroscopy following the pulsed irradiation of  $\text{PbBr}_2$  (and  $\text{PbCl}_2$  and  $\text{PbI}_2$ ) [24], this paper describes the first rate measurements using this technique, leading to absolute rate data for the atomic reactions. The high temperature reactions of the alkyl bromides are of commercial interest in view of their role in "antiknock" petrol additives for the internal combustion engine.

Fundamentally, the range of observed activation energies characterized in this investigation for various reactants may be compared, for example, with those reported recently for atomic sodium with similar molecules [21, 23]. Finally, the large activation energies that have been observed here clearly indicate that the room temperature measurements for the removal of  $\text{Pb}(6^3\text{P}_0)$  by alkyl bromides reported by Cross and Husain [12] are too high and need revision. This is discussed in the light of the measured Arrhenius parameters for the atomic reactions, including the nature of the two techniques that have been employed to obtain absolute rate data for  $\text{Pb}(6^3\text{P}_0)$  and the bond dissociation energy of  $\text{PbBr}$ .

## 2. Experimental details

The experimental arrangement essentially combines the type of high temperature reactor assembly described for the kinetic study of  $\text{Na}(3^2\text{S}_{1/2})$  [19] with the monitoring system for atomic lead used hitherto for the room temperature study with alkyl bromides [12], with some modifications. The high temperature assembly, which is heated externally by a heating tape, contains a quartz reactor with two sealed and evacuated end compartments which are heated independently to prevent condensation on the end windows and to sustain a constant temperature across the length of the reactor. Entry of gases into the reactor is controlled by means of a magnetic plug [19]. The temperatures within the reactor assembly are monitored by thermocouples which are placed on the body of the photochemical reactor, in the region of the end windows, on the entrance port and on the separately heated side arm for the addition of the solid photochemical precursor. The precursor in these measurements was the  $\text{PbBr}_2$  vapour above the solid at temperatures varying from about 640 to 760 K. The vapour pressure has been reported to obey the equation [25, 26]

$$\ln p_{\text{PbBr}_2} = 22.01 - \frac{17613}{T} \quad (1)$$

where  $p$  is in torrs (1 Torr is  $133.32 \text{ N m}^{-2}$ ;  $1 \text{ N m}^{-2}$  is 1 Pa; 1 mbar is 100 Pa) and  $T$  is in kelvins. Thus at the lower end of the temperature scale  $p_{\text{PbBr}_2} \approx 4 \text{ mTorr}$  which is a convenient pressure for the photochemical generation of  $\text{Pb}(6^3\text{P}_0)$  at densities suitable for spectroscopic monitoring using *low* photoflash energies, a fundamental requirement in these measurements (see below). The UV absorption spectrum of  $\text{PbBr}_2$  vapour has been reported for temperatures in excess of those employed here (815 - 903 K), exhibiting broad continuous absorption from  $\lambda \approx 370 \text{ nm}$  to lower wavelengths, and showing a maximum in the region  $\lambda \approx 270 \text{ nm}$  [27, 28]. Absolute extinction coefficients are quoted, but these are not considered totally reliable on account of some thermal decomposition at these temperatures [27, 28]. In the present experiment, the absolute values of  $[\text{Pb}(6^3\text{P}_0)]$  are not required for the analysis of the observed first-order kinetic decays.

The resonance absorption signals at  $\lambda = 283.3$  nm ( $\text{Pb}(7s(3P_1^{\circ})) \leftarrow \text{Pb}(6p^2(3P_0))$ ,  $gA = 1.8 \times 10^8 \text{ s}^{-1}$  [29]), were monitored in a manner similar to that described previously for the study of the reaction rates for  $\text{Pb}(6^3P_0) + \text{O}_2/\text{NO} + \text{M}$  [9], namely using a small monochromator of limited resolution (Grubb Parsons M2 monochromator) for optical isolation, in contrast to the kinetic study for the reactions between  $\text{Pb}(6^3P_0)$  and the alkyl bromides at room temperature, which employed the higher resolution Seya-Namioka instrument [12]. The source of resonance radiation again comprised a high spectral output lead hollow cathode lamp (Westinghouse, U.S.A.) operating at about 1000 V and 7 mA and monitored photoelectrically (photomultiplier tube EMI 9783B). Departures from the standard Beer-Lambert law for resonance absorption signals at  $\lambda = 283.3$  nm have been described quantitatively by Cross and Husain [11], who constructed a curve-of-growth [30] ( $I_0/I_{\text{tr}}$  versus  $[\text{Pb}(6^3P_0)]$ ) from steady resonance absorption measurements on lead vapour in equilibrium with the solid at elevated temperatures. This study made use of phase-sensitive detection and the higher resolution of the Seya-Namioka monochromator [9, 12]. Under the standard conditions of kinetic measurements, where the slit widths are widened (to not more than 0.5 mm) to monitor the time-resolved signals, contributions by atomic lead emission at  $\lambda = 282.3$  nm ( $6d(3D_2^{\circ}) \rightarrow 6p^2(3P_2)$  [31]) are not totally eliminated. Primarily for this reason the curve-of-growth calibration constructed under conditions in which the transition at  $\lambda = 283.3$  nm is optically isolated [11] cannot be sensibly applied. Accordingly, we employ the Beer-Lambert law for the resonance absorption signals; this is an approach that is supported by the resulting values of the diffusion coefficients for  $\text{Pb}(6^3P_0)$  that have been measured in some detail (see below) and which can be regarded as constituting an internal kinetic standard in these investigations.

Following the pulsed irradiation of the  $\text{PbBr}_2$  vapour the photoelectric signals due to resonance absorption at  $\lambda = 283.3$  nm were amplified without distortion using a current-to-voltage converter [32] and captured and stored using a transient recorder (Data Laboratories DL 905) that was operated in the A/B mode. The A sweep of the transient recorder records the majority of the time-resolved resonance absorption signal  $I_{\text{tr}}$  on a relatively short time scale (about 5 - 20 ms); the B sweep records the unattenuated signal  $I_0$  on a long time scale (10 s, after which all  $\text{Pb}(6^3P_0)$  has been removed). The data from the transient recorder were transferred by punched tape (Datadynamics punch 1133) to the University of Cambridge IBM 3081 computer for subsequent analysis following the procedure described by Clark and Husain [33, 34]. Combining the Beer-Lambert law with the assumption of a first-order kinetic decay of  $\text{Pb}(6^3P_0)$  yields

$$I_{\text{tr}} = I_0 \exp\{-A \exp(-k't)\} \quad (2)$$

where  $k'$  is the pseudo-first-order decay coefficient for  $\text{Pb}(6^3P_0)$  and is the parameter of kinetic interest. Computer fitting of the resonance absorption signals to eqn. (2) [33, 34] is preferable to the use of a first-order kinetic

plot (i.e.  $\ln\{\ln(I_0/I_{tr})\}$  versus  $t$ ) as it permits a much larger portion of the decay trace to be used. This is particularly apparent at the tail-end of the decay where  $I_0/I_{tr}$  tends to unity with a large accompanying scatter in the plot of  $\ln\{\ln(I_0/I_{tr})\}$  versus  $t$ . Finally, the materials, in particular the alkyl bromides, were prepared essentially as described in ref. 12 for the kinetic study of  $Pb(6^3P_0)$  with these compounds at room temperature. Solid  $PbBr_2$  (Analar) was used directly.

### 3. Results and discussion

Figure 1(a) shows an example of the digitized time variation of the transmitted light intensity at  $\lambda = 283.3$  nm ( $Pb(7^3P_1^o \rightarrow 6^3P_0)$ ) which indicates the decay of resonance absorption by ground-state lead atoms from the low-energy pulsed irradiation of  $PbBr_2$  vapour in the presence of excess

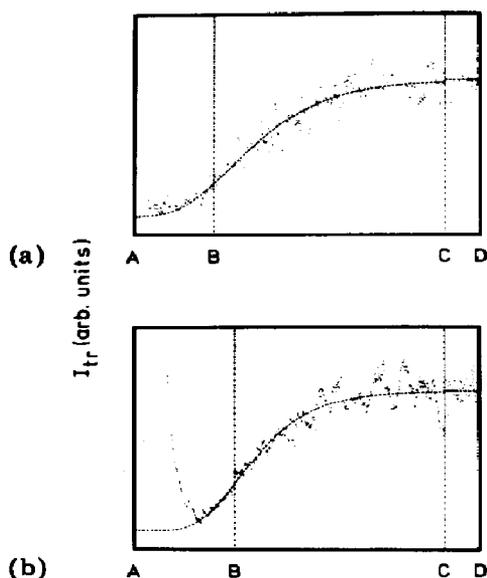


Fig. 1. Examples of the digitized time variation of the transmitted light intensity  $I_{tr}$  at  $\lambda = 283.3$  nm ( $Pb(7s(^3P_1^o) \rightarrow 6p^2(^3P_0))$ ) indicating the decay of resonance absorption by ground-state lead atoms following the pulsed irradiation of  $PbBr_2$  vapour in the presence of  $CH_2Br_2$ :  $E = 20$  J;  $p_{total\ with\ He} = 32$  mbar; abscissa labelling indicates the time base of transient recorder (AC, A sweep; CD, B sweep; BC, portion of the A sweep analysed for the kinetic decay of  $Pb(6^3P_0)$ ); dots, data points; ---, computerized fitting to the form  $I_{tr} = I_0 \exp\{-A \exp(-k't)\}$ ;  $k'$ , pseudo-first-order rate coefficient for the decay of  $Pb(6^3P_0)$ .

	$p_{CH_2Br_2}$ (mbar)	AC (ms)	CD (s)	$I_0$ (arbitrary units)	$k'$ ( $s^{-1}$ )	$T$ (K)
(a)	0	18.48	10	$168.5 \pm 19.0$	$330 \pm 50$	641
(b)	0.825	4.6	10	$148.4 \pm 15.0$	$1700 \pm 360$	688

helium at 641 K. The atom is clearly long-lived and its disappearance is governed by diffusion (see below). Portion AC of the trace comprises the A sweep of the transient recorder (18.48 ms) and CD comprises the B sweep (10 s). The decay is fitted by computer to eqn. (2) from the combination of the level of the infinite-time signal  $I_0$  of the B sweep, with the data in the portion BD analysed as a double-exponential curve (Fig. 1(a)). This was chosen to eliminate the effect of the scattered light from the photo-flash within the region AB and to limit the measurements to degrees of light absorption below about 50% to avoid effects arising from line saturation and deviations from the Beer-Lambert law. This procedure yields the parameters in eqn. (2), namely  $I_0$ ,  $A$  and  $k'$ . The ordinate in Fig. 1 is only required in arbitrary units of the transient recorder for a particular decay as  $k'$  is generated from the ratio  $I_0/I_{tr}$ . Figure 1(b) shows the effect on the decay of the addition of  $\text{CH}_2\text{Br}_2$  at a marginally elevated temperature (688 K). The variation of the diffusional loss of  $\text{Pb}(6^3\text{P}_0)$  with temperature over this range is very small (about 10%, see below). The increase in decay rate from the computed value of  $k' = 330 \pm 50 \text{ s}^{-1}$  (Fig. 1(a)) to  $k' = 1700 \pm 360 \text{ s}^{-1}$  (Fig. 1(b)) is clearly due to reaction. The scatter in the rate data  $k'$  computed from the residuals to the fitted function in Fig. 1 is somewhat large, but the rate constants  $k_{\text{RBr}}$  were determined from a large number of measurements across a significant concentration range and the resulting errors in  $k_{\text{RBr}}$  are much smaller than those indicated in individual values of  $k'$ , as expected.

Before proceeding with characterizing the absolute second-order rate constants of  $\text{Pb}(6^3\text{P}_0)$  with alkyl bromides at elevated temperatures, a comparison must be made between the nature of the present measurements and those carried out at room temperature [12]. Those measurements employed a double-walled quartz reactor, the outer annular space of which was about 1 cm thick constituting a filter. This contained the alkyl bromide at a relatively high concentration and was intended to prevent actinic radiation from photolysing  $\text{RBr}$  in the inner reaction volume where it was present at a much lower concentration and included the precursor  $\text{Pb}(\text{C}_2\text{H}_5)_4$  in an excess of helium buffer gas [12]. Ideally, the effectiveness of the filter is best considered in terms of the overlap of the light output from the flash lamp, which can be approximated to a black-body radiator at  $T = 6500 \text{ }^\circ\text{C}$  [35], and the absorption spectra of the alkyl bromides [36 - 39]. Here we shall simply consider the light transmission through the filter at absorption maxima for two of the cases described by Cross and Husain [12]. Thus, for two of the examples in the room temperature study,  $\text{CH}_2\text{Br}_2$  ( $\log_{10}\epsilon(\lambda = 225 \text{ nm}) = 3.15$ ) and  $\text{CH}_2\text{BrCH}_2\text{Br}$  ( $\log_{10}\epsilon(\lambda \approx 200 \text{ nm}) = 3.06$ ) (where  $\epsilon$  is in litres per mole per centimetre) [38], for the filter concentrations employed respectively of  $5 \times 10^{17}$  molecules  $\text{cm}^{-3}$  and  $3 \times 10^{17}$  molecules  $\text{cm}^{-3}$  [12], it is seen that  $I_{tr}(\lambda = 225 \text{ nm}, \text{CH}_2\text{Br}_2) = 7\%$  and  $I_{tr}(\lambda = 200 \text{ nm}, \text{CH}_2\text{BrCH}_2\text{Br}) = 27\%$ . The percentage of light transmission will of course be greater at other wavelengths where the light output from the black-body radiator is significant. The high temperature reactor assembly used here does

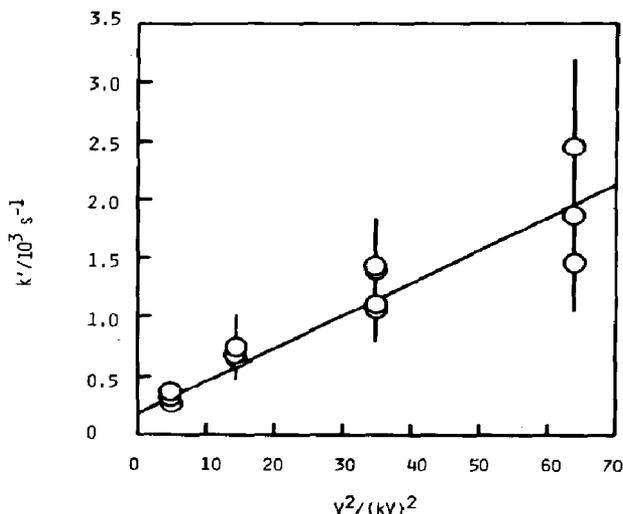


Fig. 2. Variation  $k'$  vs.  $V^2$  of the pseudo-first-order rate coefficient  $k'$  for the decay of  $\text{Pb}(6^3\text{P}_0)$  with flash energy ( $E = (1/2)CV^2$ ,  $C = 10 \mu\text{F}$ ) following the pulsed irradiation of  $\text{PbBr}_2$  vapour in the presence of 1,2-dibromoethane ( $p_{\text{C}_2\text{H}_4\text{Br}_2} = 0.3 \text{ mbar}$ ;  $p_{\text{total with He}} = 33 \text{ mbar}$ ;  $T = 616 \text{ K}$ ).

not readily permit the use of a filter. For this reason, we employed the alternative procedure of using low flash energies (*e.g.* about 20 J) compared with the higher energies used hitherto (about 140 - 160 J) [12]. An example of the effect of the flash energy for the case of  $\text{CH}_2\text{BrCH}_2\text{Br}$  is presented in Fig. 2 which shows a plot of the observed first-order decay coefficient  $k'$  against the flash energy  $E = (1/2)CV^2$ . For a given mixture,  $k'$  increases by a factor of about 7 on increasing the flash energy by a factor of about 13. For the lowest energy employed for the data in Fig. 2 (about 25 J),  $k'$  is only approximately four times the rate of that for the loss of  $\text{Pb}(6^3\text{P}_0)$  by diffusion to the walls of the reactor (see below). A further quantitative justification for the procedure of employing a low flash energy (20 J) without a filter can be seen in the resulting values of  $k_{\text{RBr}}$ . An Arrhenius extrapolation of the present rate data to room temperature yields values of  $k_{\text{RBr}}$  that are significantly *lower* than those observed hitherto [12]. Thus reactions of  $\text{Pb}(6^3\text{P}_0)$  with the photoproducts of  $\text{RBr}$  such as  $\text{Br}_2$  have essentially been minimized in the present low energy system.

### 3.1. Diffusion of $\text{Pb}(6^3\text{P}_0)$ in helium

Figure 3(a) gives an example of the variation of  $k'$  for the decay of  $\text{Pb}(6^3\text{P}_0)$  following the pulsed irradiation of  $\text{PbBr}_2$  vapour in the presence of helium alone at a given temperature (611 K) as a function of  $1/p_{\text{He}}$  and clearly demonstrates diffusional loss. Figures 3(b) - 3(d) show examples of analogous results at different temperatures. Following the procedure employed for the diffusional removal of  $\text{Na}(3^2\text{S}_{1/2})$  [19], the data of Fig. 3 and those for other temperatures were analysed using the long-time solution

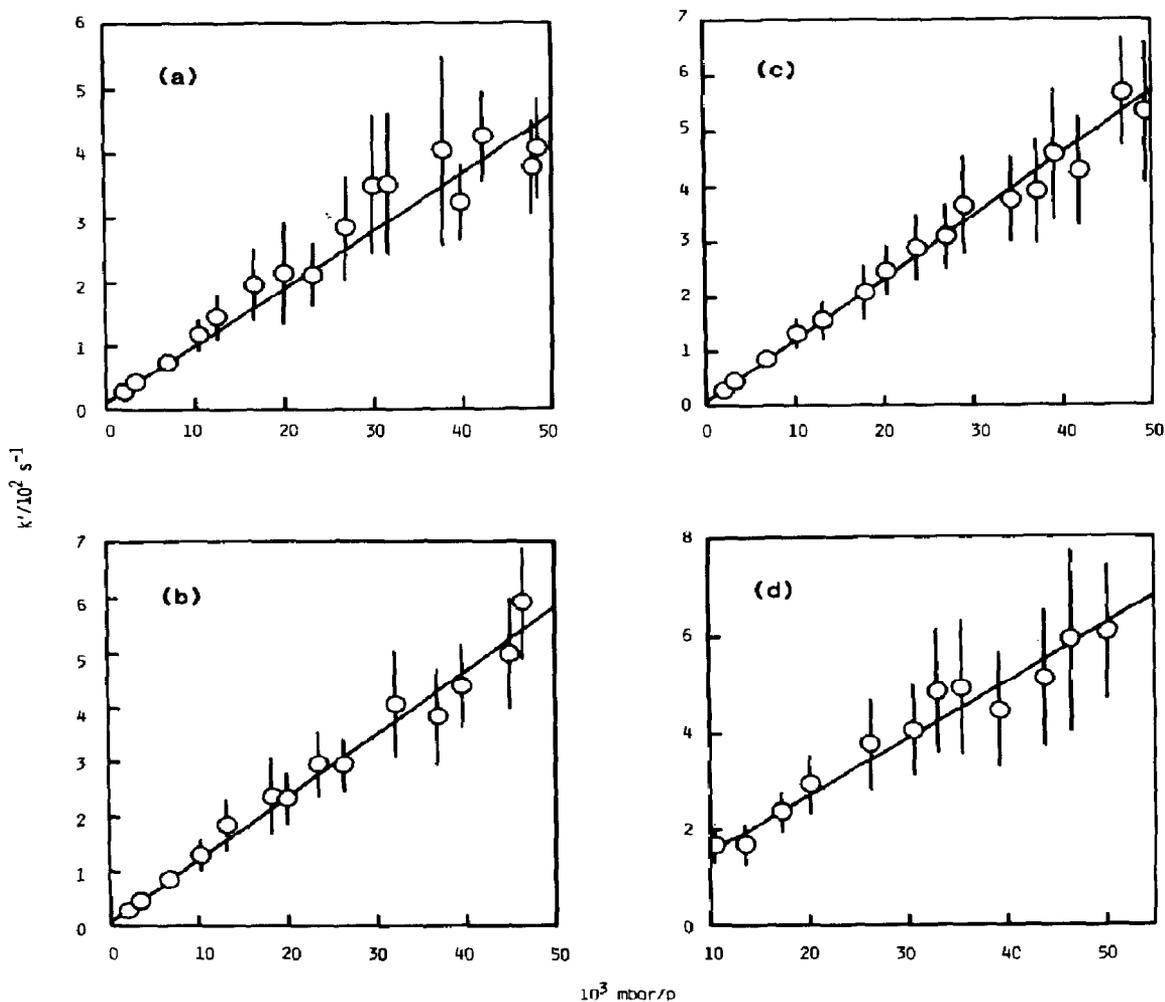


Fig. 3. Variation of the pseudo-first-order rate coefficient  $k'$  for the decay of  $\text{Pb}(6^3\text{P}_0)$  following the pulsed irradiation of  $\text{PbBr}_2$  vapour at various temperatures with the reciprocal of the pressure of helium, indicating the diffusional removal of lead atoms ( $E = 20 \text{ J}$ ): (a)  $T = 611 \text{ K}$ ; (b)  $T = 645 \text{ K}$ ; (c)  $T = 681 \text{ K}$ ; (d)  $T = 718 \text{ K}$ .

of the diffusion equation for a cylinder of radius  $r$  (here  $r = 1 \text{ cm}$ ), and length  $l$  ( $l \gg r$ ) [30, 40].

$$k' \approx \frac{5.81D_{12}}{r^2} \quad (3)$$

where  $D_{12}$  is the diffusion coefficient  $D(\text{Pb}(6^3\text{P}_0)\text{-He})$ . The diffusion of  $\text{Pb}(6^3\text{P}_0)$  in helium was investigated over the range 611 - 738 K using plots of the type shown in Fig. 3. Simple gas kinetic theory suggests a temperature dependence of the form  $D_{12} \propto T^n$  where  $n = 1.5$ . This cannot be verified by our results as the slopes of the appropriate plots in Fig. 3 would only be expected to vary by a factor of  $(738/611)^{1.5} = 1.33$  across the complete

temperature range (non-ideal gas behaviour would not significantly increase this value). Accordingly, we assume a temperature dependence for  $D_{12}$  with  $n = 1.5$ , which is in sensible accord with previous observations, *e.g.* for  $D(\text{Na}(3^2\text{S}_{1/2})-\text{N}_2)$  ( $n = 1.52 \pm 0.24$  [21]), and hence can calculate  $D(\text{Pb}(6^3\text{P}_0)-\text{He})$  at standard temperature and pressure (s.t.p.) derived from the slope of each plot. The results are given in Table 1. The data are clearly consistent, yielding a weighted average of  $D(\text{Pb}(6^3\text{P}_0)-\text{He})$  of  $0.48 \pm 0.03 \text{ cm}^2 \text{ s}^{-1}$  (at s.t.p.). This result is comparable with the recently obtained data for  $D(\text{Cl}(3^2\text{P}_J)-\text{He})$  which on extrapolation to s.t.p. gives a value of  $0.48 \pm 0.02 \text{ cm}^2 \text{ s}^{-1}$  [41], but is higher than that obtained recently for  $D(\text{Na}(3^2\text{S}_{1/2})-\text{N}_2)$  at s.t.p. of  $0.15 \pm 0.05 \text{ cm}^2 \text{ s}^{-1}$  [21]. In order to compare the diffusion coefficients measured by the present method a total removal at the walls of the reactor is assumed, whereas the sticking coefficients for the different atoms at a given surface may vary. Notwithstanding this limitation, the present measurements show that diffusion constitutes a sensible internal kinetic standard as a test of the technique, but it is not employed for relative kinetic measurements. The results support the use of the standard Beer-Lambert law for the  $\lambda = 283.3 \text{ nm}$  resonance transition as presented in Section 2.

TABLE 1

Diffusion coefficients  $D(\text{Pb}(6^3\text{P}_0)-\text{He})$  at s.t.p. derived from the slopes  $S$  of the plots of  $k'$  versus  $1/p_{\text{He}}$  at various temperatures assuming  $D(\text{Pb}(6^3\text{P}_0)-\text{He}) \propto T^{1.5}$  using the long time solution of the diffusion equation for a cylinder

$T$ (K)	$S$ ( $\times 10^3 \text{ mbar s}^{-1}$ )	$D(\text{Pb}(6^3\text{P}_0)-\text{He})$ at s.t.p. ( $\text{cm}^2 \text{ s}^{-1}$ )
611	$8.902 \pm 0.35$	$0.458 \pm 0.018$
628	$9.419 \pm 0.45$	$0.465 \pm 0.022$
645	$11.45 \pm 0.28$	$0.543 \pm 0.013$
662	$11.43 \pm 0.38$	$0.521 \pm 0.017$
681	$11.22 \pm 0.21$	$0.490 \pm 0.009$
699	$10.77 \pm 0.34$	$0.452 \pm 0.014$
718	$11.54 \pm 0.60$	$0.466 \pm 0.024$
738	$12.08 \pm 0.21$	$0.468 \pm 0.008$

The weighted average of  $D(\text{Pb}(6^3\text{P}_0)-\text{He})$  is  $0.48 \pm 0.03 \text{ cm}^2 \text{ s}^{-1}$  at s.t.p.

### 3.2. Reaction of $\text{Pb}(6^3\text{P}_0)$ with alkyl bromides

Absolute second-order rate constants for the reaction of  $\text{Pb}(6^3\text{P}_0)$  with the alkyl bromides  $\text{RBr}$  at elevated temperatures were measured from the variation of the pseudo-first-order rate coefficient  $k'$  with  $[\text{RBr}]$  (or  $p_{\text{RBr}}$ ). The data were analysed in two equivalent ways, the choice being primarily determined by the vapour pressure and the desired concentration ranges. For measurements carried out at a fixed total pressure with helium,  $k'$  can be expressed by

$$k' = K + k_{\text{RBr}}[\text{RBr}] \quad (4)$$

Hence a plot of  $k'$  versus  $[\text{RBr}]$  or  $p_{\text{RBr}}$  yields the absolute second-order rate constant  $k_{\text{RBr}}$  at a given temperature. Alternatively, a single mixture of a fixed composition  $f = p_{\text{RBr}}/(p_{\text{RBr}} + p_{\text{He}})$  is prepared. The variation of  $k'$  with different total pressures  $p$  of this mixture is then investigated. Thus, the combined loss of  $\text{Pb}(6^3\text{P}_0)$  by diffusion  $\beta$  and reaction with  $\text{RBr}$  can be expressed by

$$k' = \frac{\beta}{p} + fpk_{\text{RBr}} \quad (5)$$

(where  $k_{\text{RBr}}$  is in the appropriate units). The first term on the right-hand side of eqn. (5) can be identified with eqn. (3) as  $D_{12} \propto 1/p$ . As  $k_{\text{RBr}}$  is the

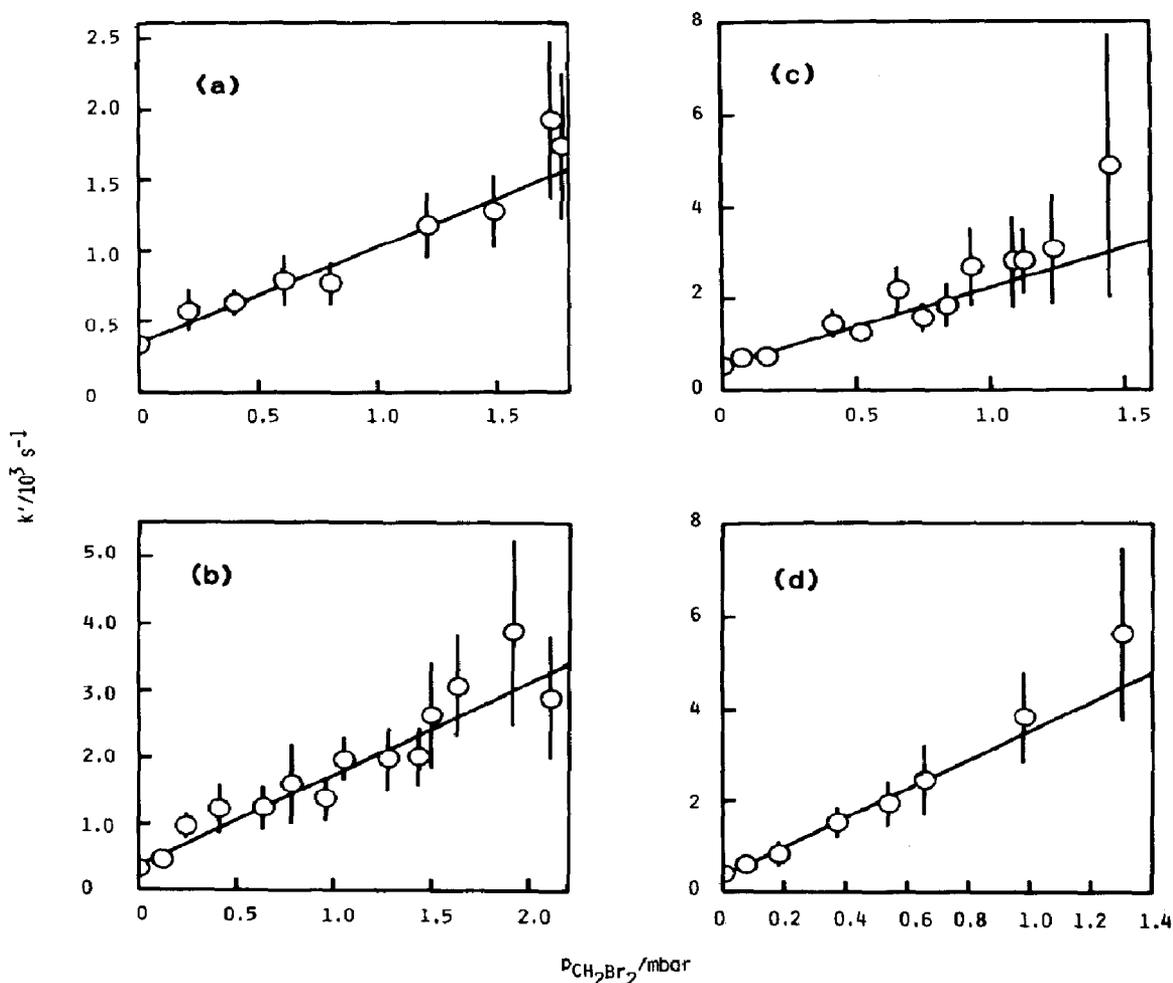


Fig. 4. Variation of  $k'$  vs.  $p_{\text{CH}_2\text{Br}_2}$  of the pseudo-first-order rate coefficient  $k'$  for the decay of  $\text{Pb}(6^3\text{P}_0)$  in the presence of dibromomethane following the pulsed irradiation of  $\text{PbBr}_2$  vapour at various temperatures ( $E = 20 \text{ J}$ ;  $p_{\text{total with He}} \approx 33 \text{ mbar}$ ): (a)  $T = 641 \text{ K}$ ; (b)  $T = 677 \text{ K}$ ; (c)  $T = 722 \text{ K}$ ; (d)  $T = 750 \text{ K}$ .

object of this investigation, eqn. (5) is rewritten as

$$k'p = \beta + fp^2k_{\text{RBr}} \quad (6)$$

Hence a plot of  $k'p$  versus  $p^2$  yields  $k_{\text{RBr}}$  through the appropriate value of  $f$ . In most cases the term  $\beta$  is small compared with  $fp^2k_{\text{RBr}}$  in these measurements and thus no major error is introduced through the determination of the second-order rate constant by what is effectively a difference technique. As both eqns. (4) and (6) are employed in this investigation, all concentrations are expressed in  $p_{\text{mbar}}$  (1 mbar is 100 Pa) in plots of (a)  $k'$  versus  $p_{\text{mbar}}(\text{RBr})$  (eqn. (4)) and (b)  $k'p_{\text{mbar}}(\text{mixture})$  versus  $p^2_{\text{mbar}}(\text{mixture})$  (eqn. (6)). Linear plots based on either eqns. (4) or (6) employed weighted least-squares analyses. For graphical data which exhibit a large scatter, the use of this procedure is reflected in the errors for the resulting Arrhenius parameters, particularly  $A$ , as expected when extrapolating the rate constant

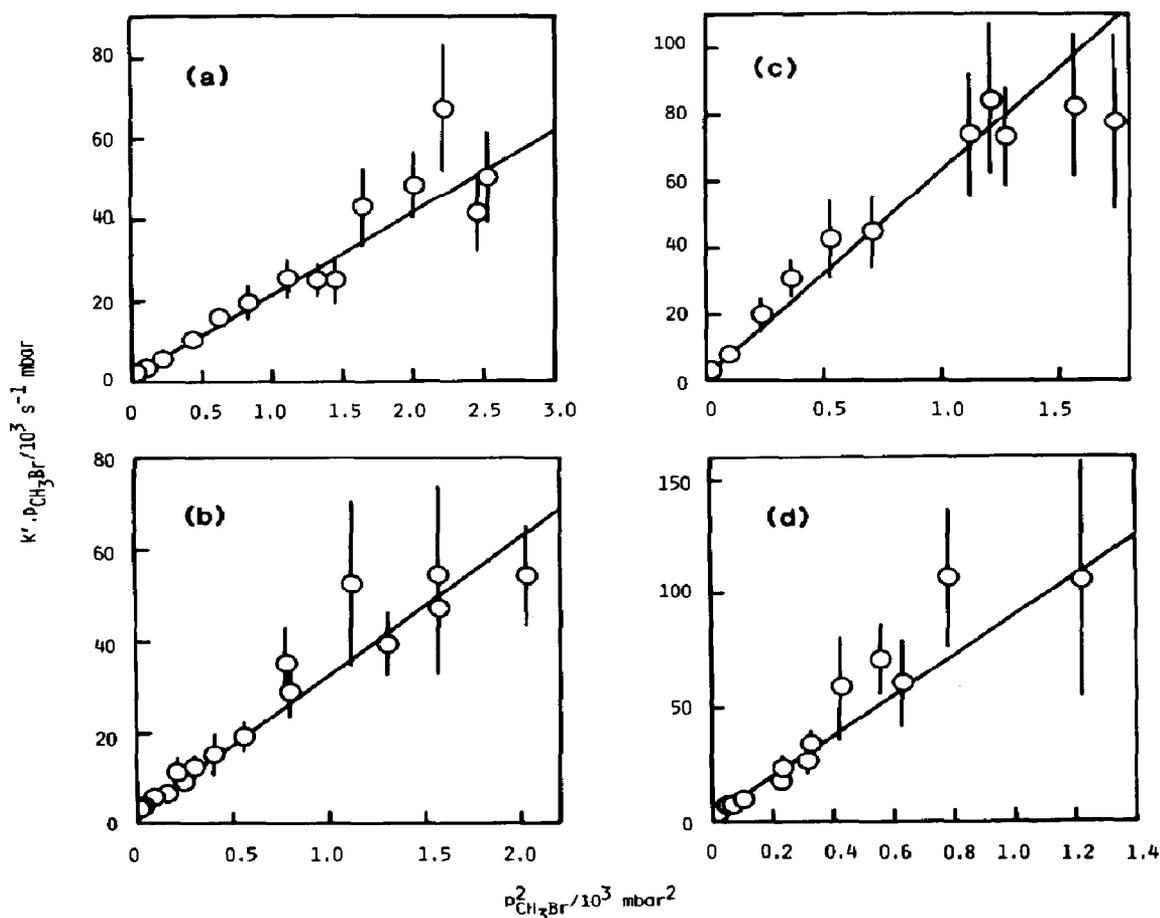


Fig. 5. Variation  $k'p_{\text{CH}_3\text{Br}}$  vs.  $p_{\text{CH}_3\text{Br}}^2$  of the pseudo-first-order rate coefficient  $k'$  for the decay of  $\text{Pb}(6^3\text{P}_0)$  in the presence of bromomethane following the pulsed irradiation of  $\text{PbBr}_2$  vapour at various temperatures indicating the removal of lead atoms by both chemical reaction and diffusion ( $E = 20 \text{ J}$ ): (a)  $T = 640 \text{ K}$ ; (b)  $T = 663 \text{ K}$ ; (c)  $T = 689 \text{ K}$ ; (d)  $T = 748 \text{ K}$ .

over a large temperature range. In general, the rate data were obtained from a large number of data points based on eqns. (4) or (6).

Figure 4 shows the variation of  $k'$  with  $p_{\text{CH}_3\text{Br}_2}$  (eqn. (4)) for four of the eight temperatures investigated; Fig. 5 demonstrates the alternative procedure of determining  $k_{\text{RBr}}$  by plotting  $k'p_{\text{CH}_3\text{Br}}$  versus  $p_{\text{CH}_3\text{Br}}^2$  and the slopes of the plots yield  $k_{\text{CH}_3\text{Br}}$  ( $f = 1$ ). In this latter case, the intercept represents the diffusion of  $\text{Pb}(6^3\text{P}_0)$  in  $\text{CH}_3\text{Br}$  itself and this is not pursued here. The intercept is, however, seen to be small on visual inspection. In fact,

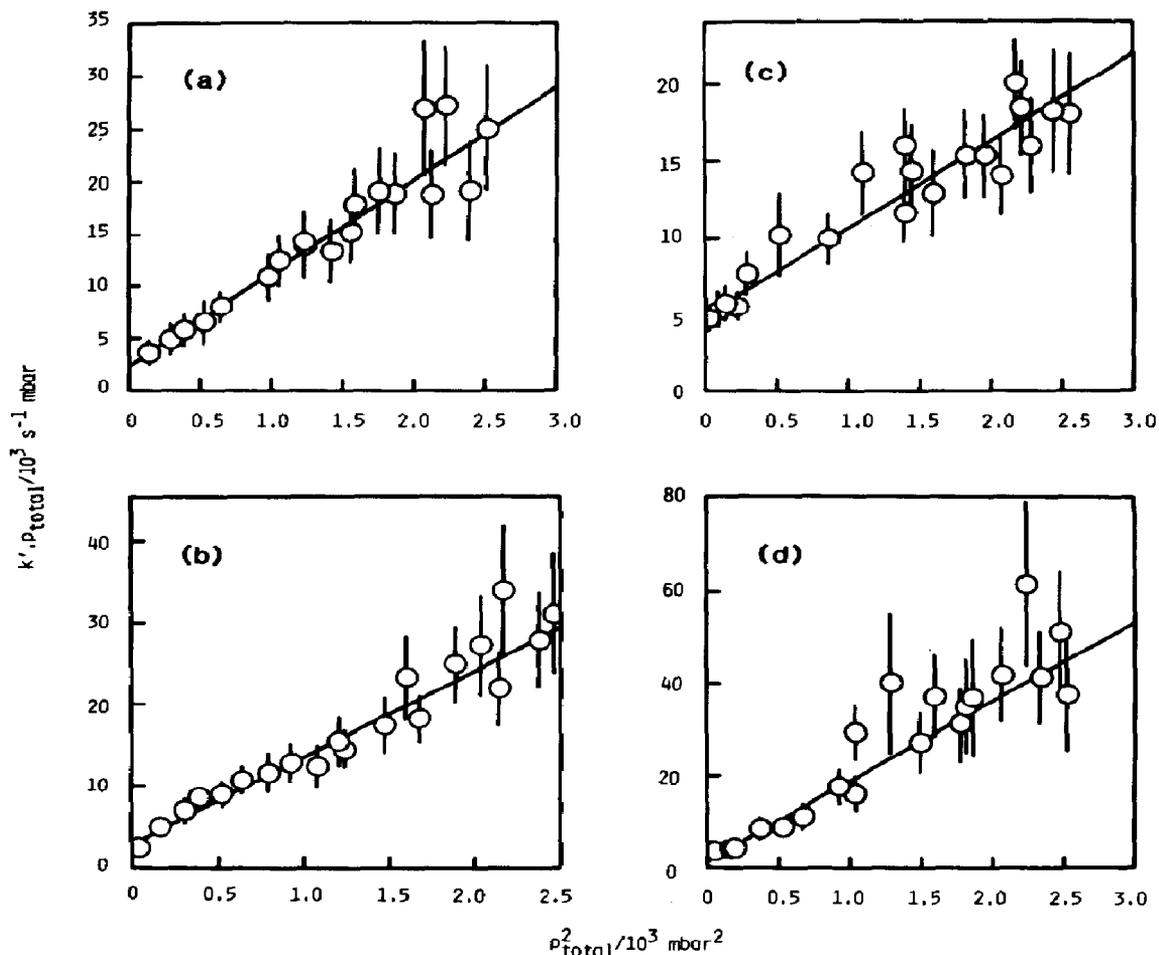


Fig. 6. Variation  $k'p_{\text{total}}$  vs.  $k'p_{\text{total}}^2$  of the pseudo-first-order rate coefficient  $k'$  for the decay of  $\text{Pb}(6^3\text{P}_0)$  in the presence of bromoethane following the pulsed irradiation of  $\text{PbBr}_2$  vapour at various temperatures ( $E = 20$  J).

	(a)	(b)	(c)	(d)
$T$ (K)	641	653	663	680
$p_{\text{C}_2\text{H}_5\text{Br}}/(p_{\text{C}_2\text{H}_5\text{Br}} + p_{\text{He}})$	0.5	0.5	0.25	0.5

for Fig. 5(a), for example, the intercept represents about 3% of the value of  $k'p_{\text{CH}_3\text{Br}}$  at the highest pressure used. Thus chemical reaction clearly dominates over diffusion. Finally, the lowest pressures of pure  $\text{CH}_3\text{Br}$  ( $f = 1$ ) employed were in the region of 7 Torr, with no significant adiabatic heating from the low-energy photoflash, this being substantiated in general by the consistency of the rate data for high pressures. Thus the slopes of the plots in Figs. 4 and 5 yield respectively  $k_{\text{CH}_2\text{Br}_2}$  and  $k_{\text{CH}_3\text{Br}}$  at the temperatures indicated in the figures.

Figure 6 gives an example ( $\text{C}_2\text{H}_5\text{Br}$ ) of the use of eqn. (6) where  $f \neq 1$ , namely  $f = 0.5$  for Figs. 6(a), 6(b) and 6(d), and  $f = 0.25$  for Fig. 6(c). In the case of  $\text{CH}_2\text{BrCH}_2\text{Br}$ , the data in the form of eqn. (4) are clearly scattered at elevated temperatures (Fig. 7) and indeed the observation of such a

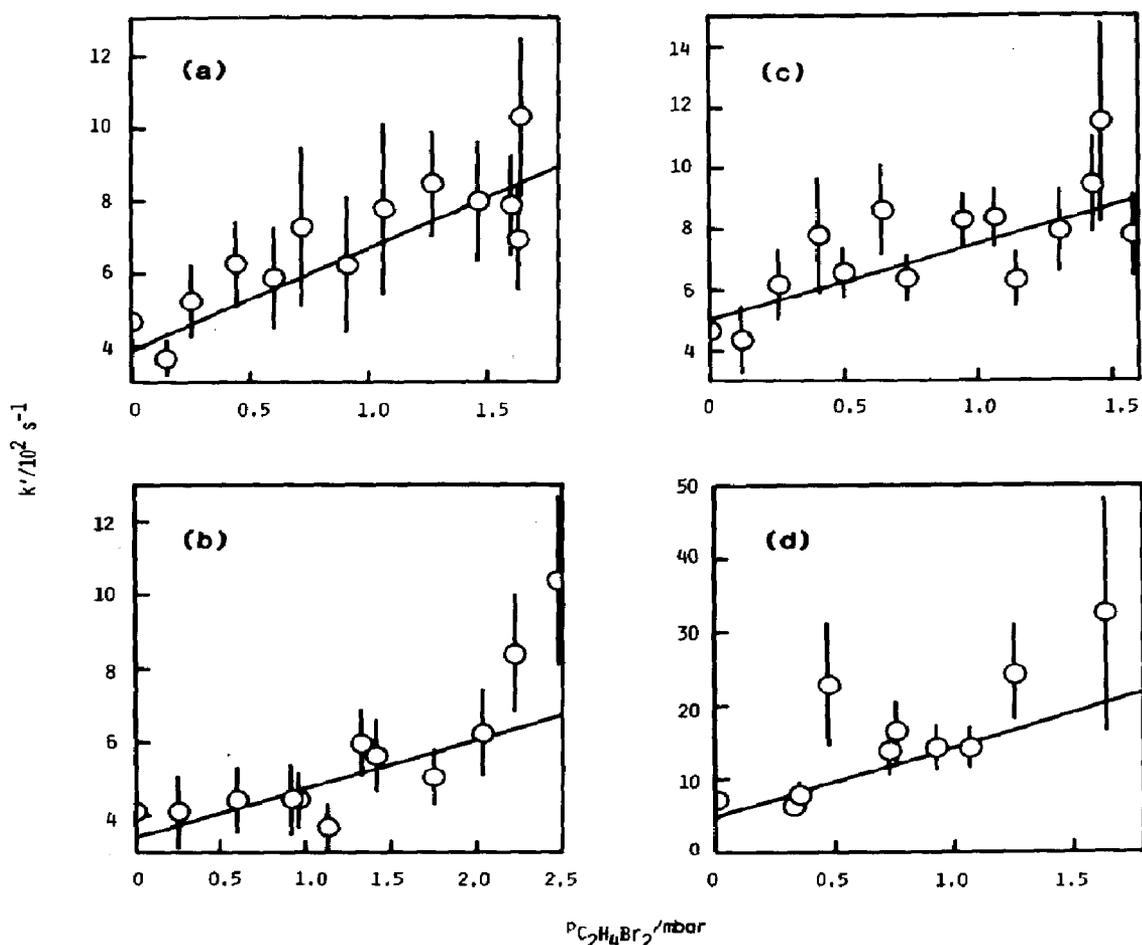


Fig. 7. Variation  $k'$  vs.  $p_{\text{C}_2\text{H}_4\text{Br}_2}$  of the pseudo-first-order rate coefficient  $k'$  for the decay of  $\text{Pb}(6^3\text{P}_0)$  in the presence of 1,2-dibromoethane following the pulsed irradiation of  $\text{PbBr}_2$  vapour at various temperatures ( $E = 20$  J;  $p_{\text{total}}$  with He  $\approx 33$  mbar): (a)  $T = 662$  K; (b)  $T = 640$  K; (c)  $T = 685$  K; (d)  $T = 743$  K.

scatter normally determines the upper limit to the temperature at which the reaction between  $\text{Pb}(6^3\text{P}_0)$  and  $\text{RBr}$  can be investigated with any confidence. Figure 8 shows the variation of  $k'$  with varying pressures of  $\text{C}_3\text{H}_7\text{Br}$ , using both eqn. (6) for the lower temperatures presented ( $T = 628 \text{ K}$  and  $665 \text{ K}$  in Figs. 8(a) and 8(b) respectively) and also eqn. (4) for the higher temperatures ( $T = 690 \text{ K}$  and  $709 \text{ K}$  in Figs. 8(c) and 8(d) respectively).

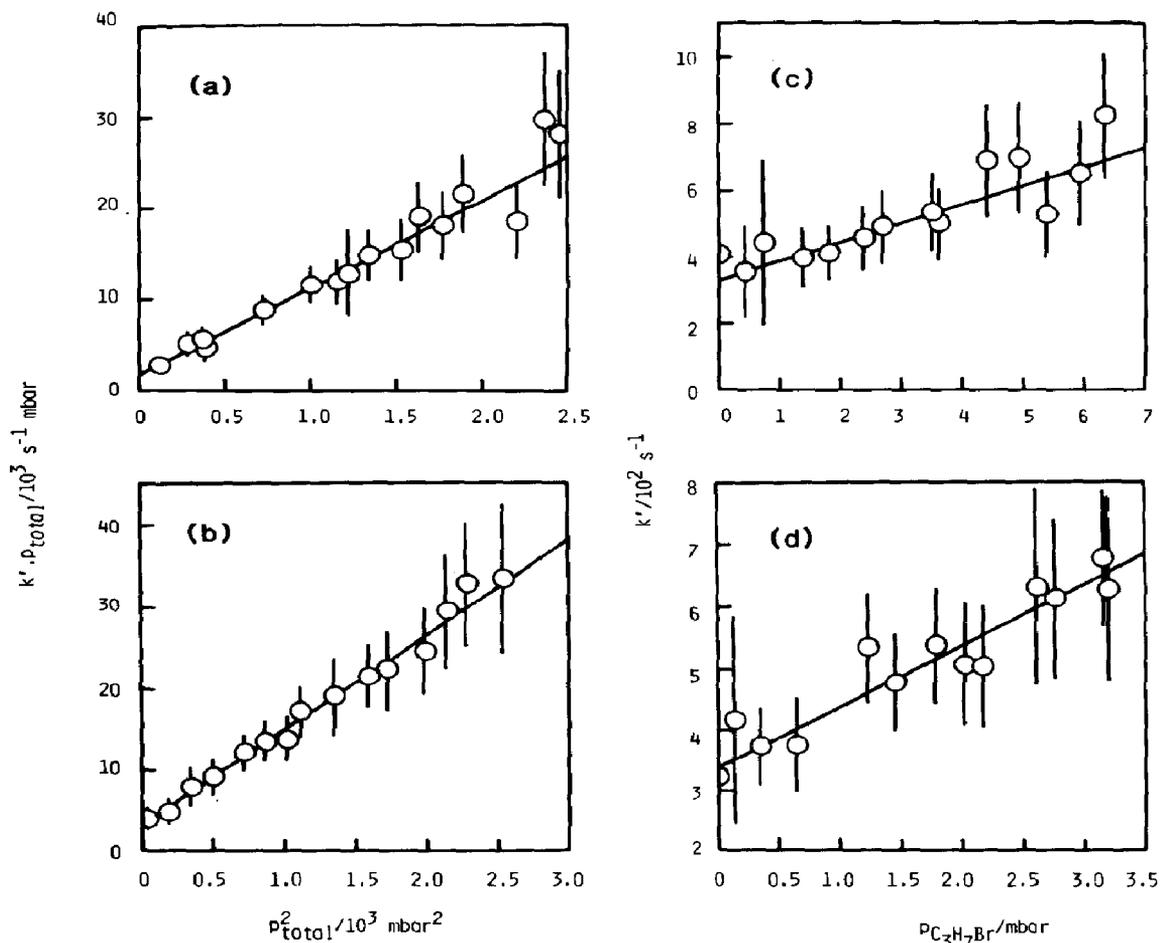


Fig. 8. Variation of the pseudo-first-order rate coefficient  $k'$  for the decay of  $\text{Pb}(6^3\text{P}_0)$  in the presence of 1-bromopropane ((a) and (b),  $k'p_{\text{total}}$  with He vs.  $k'(p_{\text{total}} \text{ with He})^2$ ; (c) and (d),  $k'$  vs.  $p_{\text{C}_3\text{H}_7\text{Br}}$ ) following the pulsed irradiation of  $\text{PbBr}_2$  vapour at various temperatures ( $E = 20 \text{ J}$ ).

	(a)	(b)	(c)	(d)
$P_{\text{C}_3\text{H}_7\text{Br}}/P_{\text{total}}$	0.45	0.25	$P_{\text{total with He}} = 33 \text{ mbar}$	$P_{\text{total with He}} = 33 \text{ mbar}$
$T \text{ (K)}$	628	665	690	709

This combination, with measurements at other temperatures, yields a consistent Arrhenius plot for the reaction of  $\text{Pb}(6^3\text{P}_0)$  with  $\text{C}_3\text{H}_7\text{Br}$  (see below).  $\text{C}_4\text{H}_9\text{Br}$  and  $\text{CH}_2\text{BrCH}_2\text{CH}_2\text{Br}$  had vapour pressures which were not sufficiently high to permit the variation of  $k_{\text{RBr}}$  with temperature to be fruitfully pursued. For these molecules, rate data are only presented for single temperatures using eqn. (6) and eqn. (4) respectively (Fig. 9).

The thermal decomposition of the alkyl bromides, to yield  $\text{Br}_2$  for example, would be expected to cause a rapid removal of the  $\text{Pb}(6^3\text{P}_0)$  [12], whereas the extrapolated data, using the Arrhenius parameters determined in this work, indicate that slower removal rates are observed than might be expected from room temperature measurements. Further, and in general, the reactant gases (RBr and helium) are admitted into the reaction vessel at a temperature of about 700 K and left for only a few seconds in order for heat transfer to bring the system to thermal equilibrium. It may readily be seen from the Arrhenius data for the thermal decomposition of the alkyl bromides [42] that the extent of decomposition is negligible.

Figures 10 and 11 show the Arrhenius plots ( $\ln k_{\text{RBr}}$  versus  $1/T$ ) for the reactions of  $\text{Pb}(6^3\text{P}_0)$  with the alkyl bromides whose rates could readily be investigated as a function of temperature ( $\text{CH}_3\text{Br}$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{C}_2\text{H}_5\text{Br}$ ,  $\text{CH}_2\text{BrCH}_2\text{Br}$  and  $n\text{-C}_3\text{H}_7\text{Br}$ ). The resulting Arrhenius parameters are presented in Table 2. The single temperature measurements indicated in Fig. 9 yield second-order absolute rate constants (errors  $1\sigma$ ) of  $k(\text{Pb}(6^3\text{P}_0) + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}) = (2.2 \pm 0.2) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  ( $T = 639 \text{ K}$ ) and  $k(\text{Pb}(6^3\text{P}_0) + \text{CH}_2\text{BrCH}_2\text{CH}_2\text{Br}) = (3.2 \pm 1.0) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  ( $T = 741 \text{ K}$ ). Estimates of activation energies for reaction with these two molecules based on Arrhenius A factors of the order of  $4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

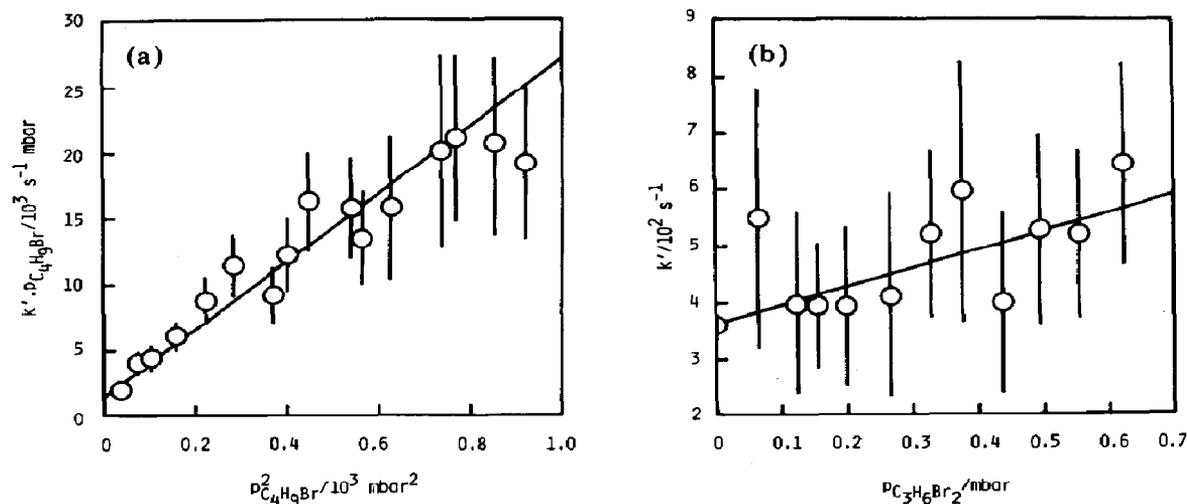


Fig. 9. Variation of the pseudo-first-order rate coefficient  $k'$  for the decay of  $\text{Pb}(6^3\text{P}_0)$  following the pulsed irradiation of  $\text{PbBr}_2$  vapour in the presence of (a) 1-bromobutane at  $T = 639 \text{ K}$  ( $k' p_{\text{C}_4\text{H}_9\text{Br}}$  vs.  $p_{\text{C}_4\text{H}_9\text{Br}}^2$ ) and (b) 1,3-dibromopropane at  $T = 740 \text{ K}$  ( $k'$  vs.  $p_{\text{C}_3\text{H}_6\text{Br}_2}$ ;  $p_{\text{total with He}} \approx 33 \text{ mbar}$ ) ( $E = 20 \text{ J}$ ).

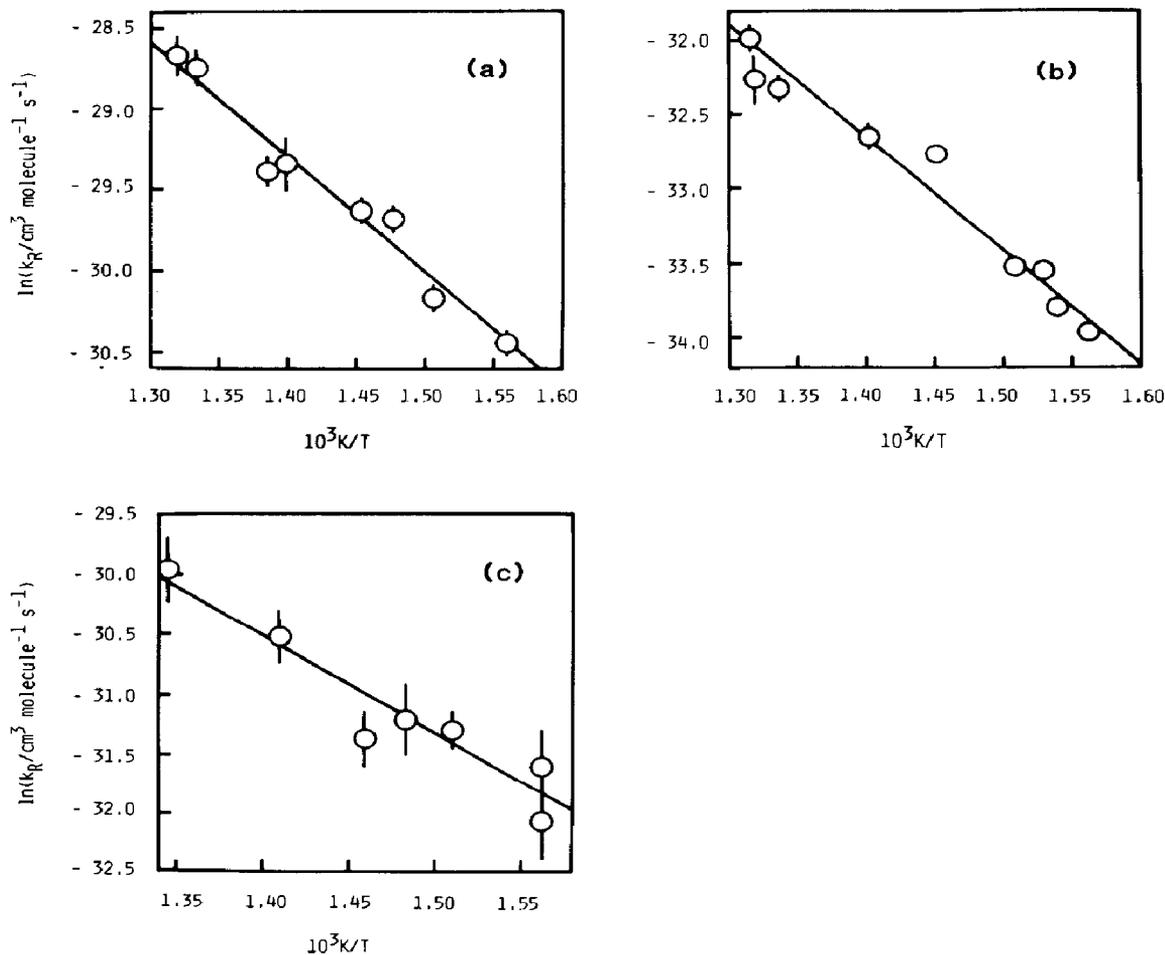


Fig. 10. Arrhenius plots ( $\ln k_R$  vs.  $1/T$ ) for the reaction of  $\text{Pb}(6^3\text{P}_0)$  with (a)  $\text{CH}_2\text{Br}_2$ , (b)  $\text{CH}_3\text{Br}$  and (c)  $\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$ .

following the data in Table 2 yield  $E(\text{Pb} + \text{C}_4\text{H}_9\text{Br}) \approx 77 \text{ kJ mol}^{-1}$  and  $E(\text{Pb} + \text{C}_3\text{H}_7\text{Br}) \approx 72 \text{ kJ mol}^{-1}$ .

We have previously considered in detail [12] the reaction endothermicities for the process



in terms of the bond energies for the various alkyl bromides, determined by a variety of methods [43 - 54], including the uncertainty in  $D(\text{Pb}-\text{Br}) = 2.5 \pm 0.4 \text{ eV}$  [55, 56] arising from the analysis of the predissociation in the spectrum of  $\text{PbBr}$  reported by Wieland and Newburgh [57]. Given the similarity between the activation energies for the reactions with  $\text{Pb}(6^3\text{P}_0)$  and the bond energies of the alkyl bromides, we shall only consider the reaction thermochemistry for the simplest case, namely  $\text{CH}_3\text{Br}$ , where  $D(\text{CH}_3-\text{Br}) = 70.0 \pm 1.2 \text{ kcal mol}^{-1}$  [50 - 52]. Using the above value for

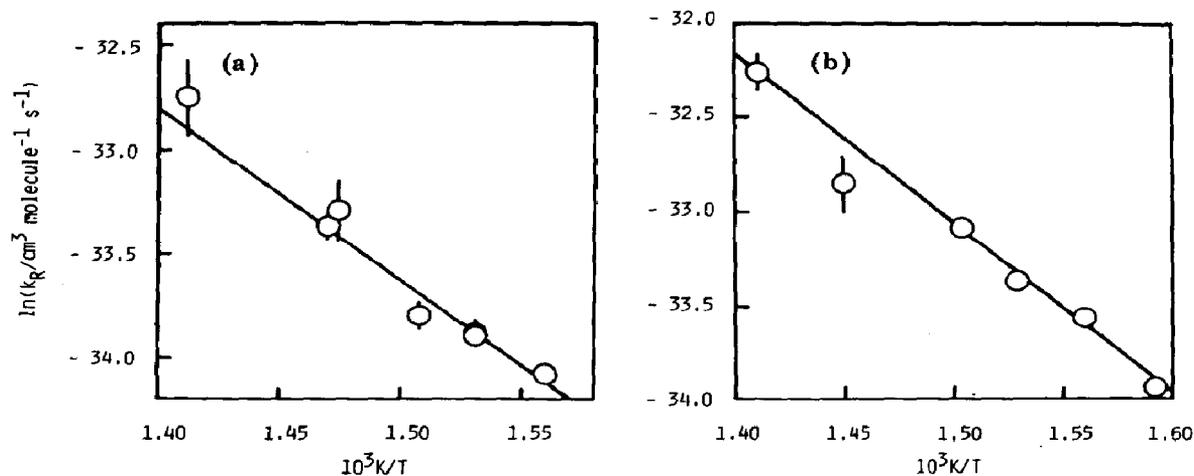


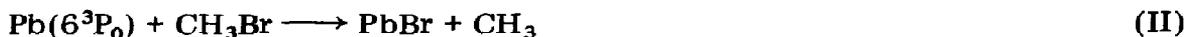
Fig. 11. Arrhenius plots ( $\ln k_R$  vs.  $1/T$ ) for the reaction of  $\text{Pb}(6^3\text{P}_0)$  with (a)  $\text{C}_2\text{H}_5\text{Br}$  and (b)  $n\text{-C}_3\text{H}_7\text{Br}$ .

TABLE 2

Arrhenius parameters  $k_{\text{RBr}} = A \exp(-E/RT)$  for the reaction of  $\text{Pb}(6^3\text{P}_0)$  with alkyl bromides determined by time-resolved atomic resonance absorption spectroscopy following the pulsed irradiation of  $\text{PbBr}_2$  vapour at elevated temperatures (errors  $1\sigma$ )

<i>RBr</i>	$A$ ( $\times 10^{-10}$ $\text{cm}^3$ molecule $^{-1}$ s $^{-1}$ )	$E$ (kJ mol $^{-1}$ )	Temperature range (K)
$\text{CH}_3\text{Br}$	$3.0^{+1.0}_{-1.7}$	$63.6 \pm 4.8$	640 - 760
$\text{CH}_2\text{Br}_2$	$39^{+59}_{-13}$	$59.0 \pm 5.1$	641 - 758
$\text{C}_2\text{H}_5\text{Br}$	$5.6^{+11}_{-3.8}$	$68.3 \pm 6.2$	641 - 708
$\text{CH}_2\text{BrCH}_2\text{Br}$	$46^{+28}_{-2.0}$	$67.2 \pm 11.1$	640 - 743
$n\text{-C}_3\text{H}_7\text{Br}$	$31^{+38}_{-17}$	$74.5 \pm 4.3$	628 - 709

$D(\text{PbBr})$  [55, 56], we see that for the reaction



$\Delta H = 12 \pm 10$  kcal mol $^{-1}$  [56] (1 kcal is 4.18 kJ; 1 eV is 23.061 kcal mol $^{-1}$ ; 0.1 eV is about 10 kJ mol $^{-1}$ ) which is compatible with the observed activation energy ( $63.6 \pm 4.8$  kJ mol $^{-1}$ , Table 2). Indeed, we may use the observed activation energies for reactions between  $\text{Pb} + \text{CH}_3\text{Br}$  and  $\text{Pb} + \text{C}_2\text{H}_5\text{Br}$  especially (Table 2), in view of the more recent bond energy determinations, of  $D(\text{CH}_3\text{-Br})$  [50 - 52] and  $D(\text{C}_2\text{H}_5\text{-Br}) = 67.8 \pm 1.5$  kcal mol $^{-1}$  [50 - 53], to determine  $D(\text{Pb-Br})$  more accurately. These yield upper limits of 2.38 eV and 2.28 eV respectively. The rate data for  $\text{Pb} + \text{CH}_2\text{Br}_2$  (Table 2) coupled with the estimate of  $D(\text{CH}_2\text{Br-Br}) \approx 67 \pm 5$  kcal mol $^{-1}$  [50, 51] yield an upper limit of 2.46 eV. Whilst the activation energies for reaction between lead and  $\text{RBr}$  result from measurements over a limited temperature range, the resulting accuracy in the data (Table 2) leads to the safe conclusion that  $D(\text{PbBr}) \leq 2.5$  eV.

We may note that the observed activation energies for reaction between lead and RBr (Table 2) are significantly lower than those derived from the analogous single temperature rate constants for the reactions of atomic sodium in diffusion flame measurements [58], as expected on the basis of the bond energy of NaBr ( $D_0^\circ(\text{NaBr}(\text{X}^1\Sigma^+)) = 3.74 \text{ eV}$  [55]). Finally, extrapolation of the observed Arrhenius data to room temperatures indicates that the reported single room temperature values of  $k_{\text{RBr}}$  [12] are too high and that the relatively rapid decays observed for  $\text{Pb}(6^3\text{P}_0)$  presumably resulted from reactions with photofragments. The consistency of the activation energies observed here with the thermochemistry indicated above adds further weight to the rate data obtained in this investigation. In practical terms, the use of brominated compounds in antiknock petrol additives is only effective at the adiabatic flame temperatures of the internal combustion engine, certainly in terms of removal of atomic lead by bromine atom abstraction with the accompanying thermal decomposition of the alkyl bromides themselves at these temperatures [42].

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