

REACTIONS OF GROUND STATE LEAD ATOMS $Pb(6^3P_0)$ WITH ALKYL BROMIDES STUDIED BY ATOMIC ABSORPTION SPECTROSCOPY

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Summary

We present a kinetic study of the collisional removal of ground state lead atoms $Pb(6^3P_0)$ by alkyl bromides. $Pb(6^3P_0)$ was generated by the pulsed irradiation of $Pb(C_2H_5)_4$ and monitored photoelectrically by resonance line absorption at $\lambda = 283.3$ nm ($Pb(7s(^3P_1^0)) \leftarrow Pb(6p^2(^3P_0))$). We report the following second order absolute rate constants k_R for the reaction (in cm^3 molecule $^{-1}$ s $^{-1}$ at 300 K): CH_3Br , $3.7 \pm 0.5 \times 10^{-15}$; C_2H_5Br , $5.0 \pm 0.5 \times 10^{-15}$; CH_2BrCH_2Br , $5.3 \pm 0.3 \times 10^{-14}$; CH_2Br_2 , $1.4 \pm 0.2 \times 10^{-13}$; CH_3CHBr_2 , $6.0 \pm 0.5 \times 10^{-13}$; HBr , less than 10^{-15} . The rate constants are discussed in terms of the thermochemical data pertinent to Br atom abstraction and also in terms of a Hammett relationship.

Introduction

Systematic studies of the rates of chemical reactions of heavy metal atoms in their electronic ground states have not been so frequent as those for light non-metallic atoms [1, 2] although the subject has received impetus in recent years as a result of the search for molecular electronic transition lasers operating in the visible region of the spectrum and arising from heavy atom-molecule reactions [3]. Part of this development in heavy atom reaction kinetics has included the investigation of rate processes by generating such atoms by pulsed irradiation and by monitoring these transient species either in absorption using time resolved attenuation of atomic resonance radiation or by time resolved resonance fluorescence following optical excitation. The kinetics of ground state bismuth $Bi(6^4S_{3/2})$ and antimony $Sb(5^4S_{3/2})$ atoms, for example, have been studied by both techniques [4 - 7]. With particular reference to ground state lead atoms $Pb(6^3P_0)$, we have recently presented a detailed investigation of the third order processes $Pb + O_2 + M \rightarrow$ products and $Pb + NO + M \rightarrow$ products [8] for a wide range of third bodies M following

the preliminary work of Husain and Littler [9, 10]. In this paper we describe the reaction rates for the removal of $\text{Pb}(6^3\text{P}_0)$ by some alkyl bromides. Apart from their contribution to the fundamental body of knowledge of rate processes for heavy atoms, such measurements bear closely upon various steps involved in the removal of lead atoms in the internal combustion engine to which antiknock material has been added, including lead tetraethyl PbEt_4 and ethylene dibromide (1,2-dibromoethane, $\text{CH}_2\text{BrCH}_2\text{Br}$).

Experimental

The details of the experimental arrangement for monitoring ground state lead atoms in the single-shot time resolved mode following flash photolysis have been given previously [8]. The same apparatus was employed in this study with some modifications. $\text{Pb}(6^3\text{P}_0)$ was generated by the pulsed irradiation of PbEt_4 in the presence of excess helium buffer gas to prevent a significant temperature rise on photolysis and was monitored photoelectrically by resonance absorption at $\lambda = 283.3 \text{ nm}$ ($\text{Pb}(7s(3\text{P}_1^0)) \leftarrow \text{Pb}(6p^2(3\text{P}_0))$), $gA = 1.8 \times 10^8 \text{ s}^{-1}$ [11], the atomic line being derived from a hollow cathode source (High Spectral Output, Westinghouse, U.S.A.). Unlike the previous studies which employed a coaxial lamp and vessel assembly [8], the present investigation involved the use of a standard photolytic flash lamp ($l \approx 40 \text{ cm}$) with a double-walled high purity quartz (Spectrosil) reaction vessel ($l \approx 40 \text{ cm}$). The inner cylinder (internal diameter, 22 mm) constituted the reaction vessel, and the annular space (about 10 mm) constituted the filter volume into which was placed a relatively high pressure of the appropriate bromide RBr (or Br_2) to prevent direct photolysis of the low pressure of the bromide in the reaction vessel itself. Whilst the lower wavelength limit for transmission by Spectrosil is $\lambda \approx 160 \text{ nm}$, the air gap between the photolysis lamp and the double-walled reaction vessel limited photolytic radiation to $\lambda \gtrsim 185 \text{ nm}$. The other modification to the apparatus described previously involves the use of a Seya-Namioka grating monochromator [12, 13] to isolate the Pb resonance line. This instrument, which was constructed in this laboratory [14] (radius of curvature of grating, 500 mm, blaze wavelength, 110 nm, 1180 lines mm^{-1} , MgF_2 coated), has a higher resolving power than that used earlier [8]. The attenuated resonance radiation was detected by means of a photomultiplier (EMI 9783B) mounted on the exit slit of the grating monochromator.

The photoelectric pulses representing resonance absorption were then handled as previously described [8]. Thus they were amplified without distortion [15] and transferred to a transient recorder (Data Laboratories Model 905) using the two time bases in the A/B mode in order to monitor the unattenuated signal I_0 (200 digitized points) over a much longer time scale than that for the attenuated signal I_{tr} (824 digitized points). The signals were then punched onto paper tape in ASCII code (Datadynamics punch 1133) for direct input into an IBM 370 computer and smoothed in the analy-

sis according to the procedure of Savitsky and Golay [16]. We employed the modified Beer-Lambert law [17]

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

for the $\lambda = 283.3$ nm resonance transition using $\gamma = 0.38 \pm 0.04$ [9]. The use of this value of γ has been discussed in detail previously [8].

The UV spectra of the Br-containing molecules employed here have essentially been reported previously (CH_3Br , $\text{C}_2\text{H}_5\text{Br}$ [18], CH_2Br_2 , $\text{CH}_2\text{BrCH}_2\text{Br}$ [19], Br_2 , HBr [20]), though we did not locate an obvious reference to that for CH_3CHBr_2 whose spectrum we recorded on a Pye Unicam Spectrophotometer (SP8000; $\lambda_{\text{max}} \approx 220$ nm, $\log_{10}\epsilon(220 \text{ nm}) (1 \text{ m}^{-1} \text{ cm}^{-1}) \approx 3.75$). The alkyl bromides in particular exhibit broad band absorption spectra in the UV which partially overlies that of PbEt_4 [21]. Hence, concentrations of PbEt_4 , higher (by about a factor of 10) than those employed previously [8], were required in these studies in order to generate concentrations of $\text{Pb}(6^3\text{P}_0)$ suitable for attenuation measurements following photolysis of PbEt_4 after passage of the actinic radiation through the appropriate filter material. The use of higher flash energies to increase the initial yield of $\text{Pb}(6^3\text{P}_0)$ would suffer from the disadvantage of increasing the extent of any photolysis of the bromide in the reaction vessel.

Materials

PbEt_4 , He and Kr (for the photolysis lamp) were employed as described previously [8]. All the Br-containing materials, CH_3Br (BDH), $\text{C}_2\text{H}_5\text{Br}$ (BDH), CH_2Br_2 (BDH), $\text{CH}_2\text{BrCH}_2\text{Br}$ (BDH), CH_3CHBr_2 (BDH), Br_2 (Analar) and HBr (Matheson), were initially thoroughly degassed by several freeze-pump-thaw (FPT) cycles at liquid nitrogen temperature (-196 °C). CH_3Br was subsequently fractionally distilled from an n-pentane slush (-159 °C) to -196 °C. $\text{C}_2\text{H}_5\text{Br}$ was fractionally distilled from a CO_2 - $\text{C}_2\text{H}_5\text{OH}$ slush (-78 °C) to -196 °C. CH_2Br_2 was further degassed at -78 °C and then fractionally distilled from a CCl_4 slush (-23 °C) to -196 °C. $\text{CH}_2\text{BrCH}_2\text{Br}$ was further degassed at -78 °C. CH_3CHBr_2 was also degassed further at -78 °C and fractionally distilled from room temperature to -196 °C. Br_2 was similarly further degassed at -78 °C. HBr was dispensed from a bulb with a cold finger maintained at -78 °C in order to retain any Br_2 present. All the Br-containing species were degassed again at -196 °C immediately prior to preparation of the reaction mixtures. Materials for the filter jacket were simply subjected to the initial FPT cycles at -196 °C.

Results and discussion

Figure 1(a) gives an example of the computerized form of the raw data for the transmitted light intensity at $\lambda = 283.3$ nm indicating the decay of resonance absorption by $\text{Pb}(6^3\text{P}_0)$ following the pulsed irradiation of PbEt_4 . Figure 1(b) shows the effect of the data smoothing procedure of Savitsky and

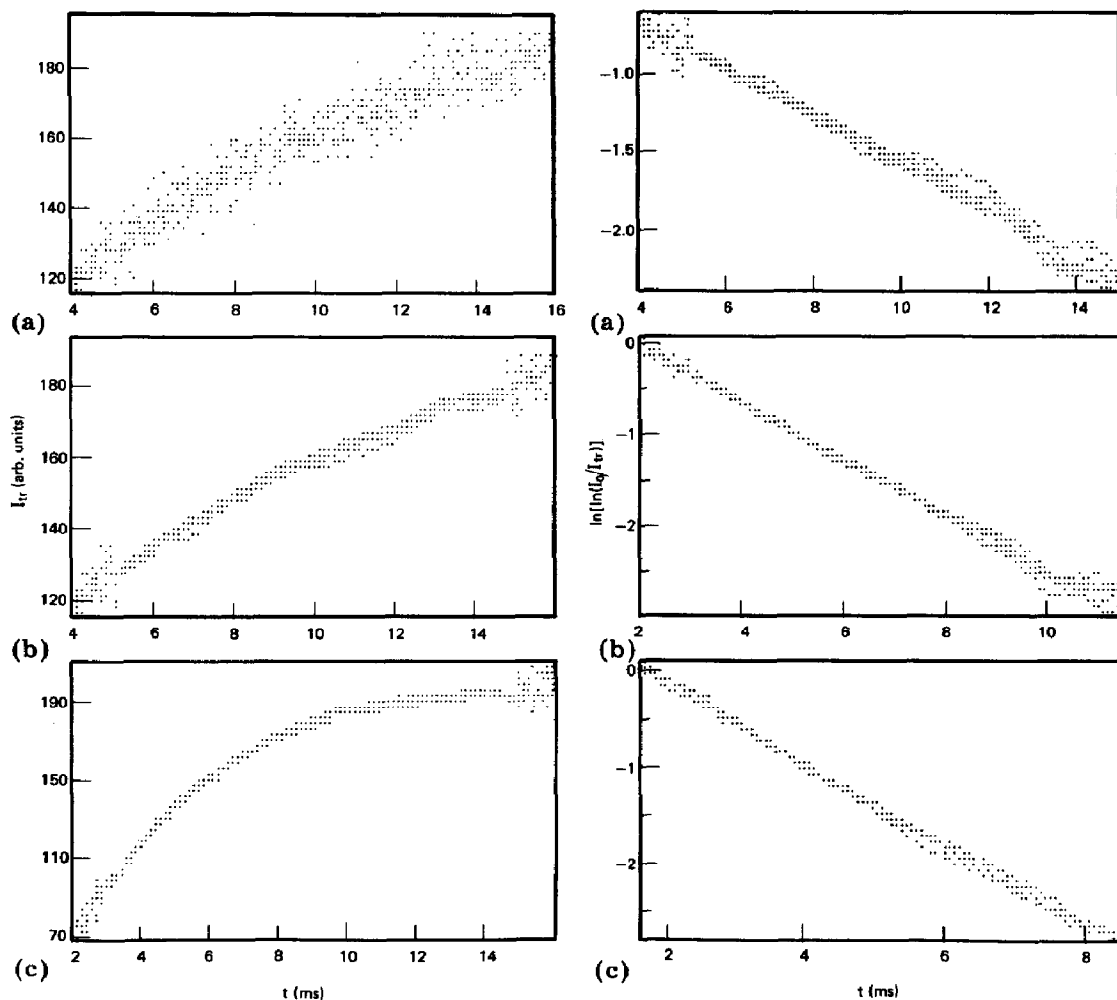


Fig. 1. Digitized time variation of the transmitted light intensity at $\lambda = 283.3$ nm ($\text{Pb}(7s^3P_1^0) \leftarrow \text{Pb}(6p^2^3P_0))$ indicating the decay of resonance absorption by ground state lead atoms. $p(\text{PbEt}_4) = 4.3 \times 10^{14}$ molecules cm^{-3} ; $p(\text{He}) = 1.1 \times 10^{18}$ atoms cm^{-3} ; $E = 122$ J; $p(\text{CH}_2\text{BrCH}_2\text{Br})$ (filter) = 3.2×10^{17} molecules cm^{-3} . $p(\text{CH}_2\text{BrCH}_2\text{Br})$ (reaction vessel, molecules cm^{-3}): (a) 0.0 (unsmoothed); (b) 0.0 (smoothed); (c) 6.6×10^{15} (smoothed).

Fig. 2. Typical pseudo first-order plots for the decay of $\text{Pb}(6^3P_0)$ obtained by monitoring the absorption of light at $\lambda = 283.3$ nm ($\text{Pb}(7s^3P_1^0) \leftarrow \text{Pb}(6p^2^3P_0))$. $p(\text{PbEt}_4) = 4.3 \times 10^{14}$ molecules cm^{-3} ; $p(\text{He}) = 1.1 \times 10^{18}$ atoms cm^{-3} ; $E = 122$ J; $p(\text{CH}_2\text{BrCH}_2\text{Br})$ (filter) = 3.2×10^{17} molecules cm^{-3} . $p(\text{CH}_2\text{BrCH}_2\text{Br})$ (reaction vessel, molecules cm^{-3}): (a) 0.0; (b) 6.6×10^{15} ; (c) 1.3×10^{16} .

Golay [16] on the data of Fig. 1(a). Figure 1(c) shows the effect on the lifetime of $\text{Pb}(6^3P_0)$ by the addition of ethylene dibromide with a relatively high pressure of this material in the filter jacket, preventing direct photolysis of the bromide. Examples of computerized plots of first order decays derived from smoothed plots of the type given in Figs. 1(b), (c) are given in Figs. 2(a) - (c), indicating the effect of ethylene dibromide. The errors in the slopes of

such plots are clearly very low, typically about 1%, the slopes being given by $-\gamma k'$, following eqn. (1), where k' is the overall first order coefficient for the decay of $\text{Pb}(6^3\text{P}_0)$ in the presence of the bromide RBr . γ is given above (0.38 ± 0.04). k' may be expressed in the form

$$k' = K + k_{\text{R}}[\text{RBr}] \quad (2)$$

K is sensibly constant in a series of experiments in which $[\text{RBr}]$ is varied owing principally to the removal of $\text{Pb}(6^3\text{P}_0)$ by undissociated PbEt_4 and by products of the photolysis of this parent molecule. k_{R} is the absolute second order rate constant for the reaction of $\text{Pb}(6^3\text{P}_0)$ with RBr . Figures 3 and 4 show the variation of k' (in fact $\gamma(k' - K)$ in order to normalize the measured rates with respect to the blank K ($[\text{RBr}] = 0$) for each set of experiments) with the concentrations of the molecules CH_3Br , $\text{C}_2\text{H}_5\text{Br}$, CH_2Br_2 and $\text{CH}_2\text{BrCH}_2\text{Br}$ using eqn. (2). The slopes of the plots given in Figs. 3 and 4, with the above value of γ , yield the appropriate absolute rate constants for reaction.

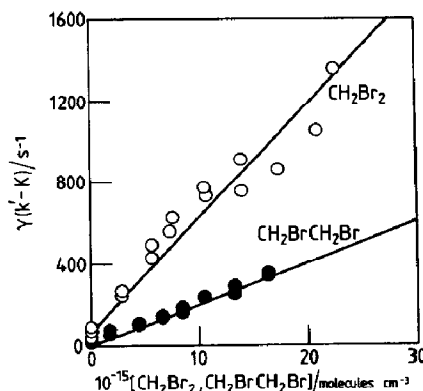
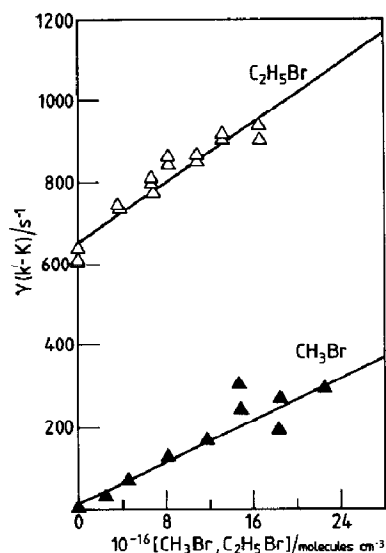


Fig. 3. Pseudo first order rate coefficients ($\gamma(k' - K)$) for the decay of $\text{Pb}(6^3\text{P}_0)$ in the presence of CH_3Br and $\text{C}_2\text{H}_5\text{Br}$. $[\text{PbEt}_4] = 2.9 \times 10^{14}$ molecules cm^{-3} , $[\text{He}] = 1.1 \times 10^{18}$ atoms cm^{-3} ; $[\text{CH}_3\text{Br}]$ (filter) = 3.3×10^{18} molecules cm^{-3} ; $E = 106$ J; $[\text{C}_2\text{H}_5\text{Br}]$ (filter) = 2.9×10^{18} molecules cm^{-3} ; $E = 303$ J; ($\gamma(k' - K) + 600$ s $^{-1}$ for $\text{C}_2\text{H}_5\text{Br}$).

Fig. 4. Pseudo first order rate coefficients ($\gamma(k' - K)$) for the decay of $\text{Pb}(6^3\text{P}_0)$ in the presence of CH_2Br_2 and $\text{CH}_2\text{BrCH}_2\text{Br}$. $[\text{He}] = 1.1 \times 10^{18}$ atoms cm^{-3} ; $E = 123$ J; $[\text{CH}_2\text{Br}_2]$ (filter) = 5×10^{17} molecules cm^{-3} ; $[\text{PbEt}_4] = 3.2 \times 10^{13}$ molecules cm^{-3} ; $[\text{CH}_2\text{BrCH}_2\text{Br}]$ (filter) = 3×10^{17} molecules cm^{-3} ; $[\text{PbEt}_4] = 4.3 \times 10^{14}$ molecules cm^{-3} .

The rate data for CH_3CHBr_2 showed anomalous behaviour as indicated by the variation of k' ($\gamma k'$) with $[\text{CH}_3\text{CHBr}_2]$ (Fig. 5). The results would appear to indicate a back reaction yielding $\text{Pb}(6^3\text{P}_0)$ whose rate increases with increasing $[\text{CH}_3\text{CHBr}_2]$. One empirical procedure would be to take the initial

slope of Fig. 5 to obtain $k(\text{CH}_3\text{CHBr}_2)$. Another empirical procedure is to express the removal rate of $\text{Pb}(6^3\text{P}_0)$ in the form

$$-\frac{d \ln[\text{Pb}(6^3\text{P}_0)]}{dt} = k' = \frac{\alpha [\text{CH}_3\text{CHBr}_2]}{1 + \beta [\text{CH}_3\text{CHBr}_2]} \quad (3)$$

Hence, on the basis of eqns. (1) - (3) a plot of $[\text{CH}_3\text{CHBr}_2]/\gamma(k' - K)$ versus $[\text{CH}_3\text{CHBr}_2]$ should be linear. This is shown in Fig. 6. The intercept of Fig. 6 yields a value of α whose magnitude is in sensible accord with that derived from the initial slope of Fig. 5 and is attributed to $k(\text{CH}_3\text{CHBr}_2)$. Such a procedure for determining α , of course, employs all the rate data rather than restricting the determination of the reaction rate constant solely to rates measured at low $[\text{CH}_3\text{CHBr}_2]$. That α may be attributed to $k(\text{CH}_3\text{CHBr}_2)$ is also supported by a comparison of its magnitude with that for the similar *gem*-dibromo compound CH_2Br_2 (*vide infra* Table 1) which did not exhibit anomalous behaviour.

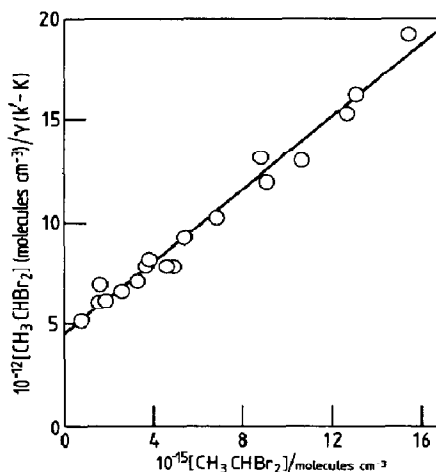
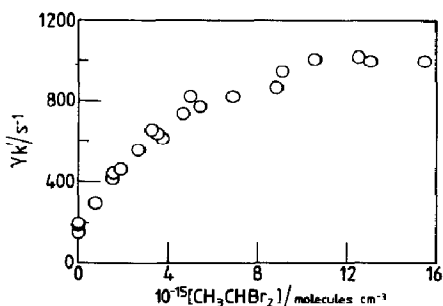


Fig. 5. Pseudo first order rate coefficients ($\gamma k'$) for the decay of $\text{Pb}(6^3\text{P}_0)$ in the presence of CH_3CHBr_2 . $[\text{PbEt}_4] = 4.3 \times 10^{14}$ molecules cm^{-3} ; $[\text{He}] = 1.1 \times 10^{18}$ atoms cm^{-3} ; $E = 141$ J. $[\text{CH}_3\text{CHBr}_2]$ (filter) = 3×10^{17} molecules cm^{-3} .

Fig. 6. Determination of the initial rate for the decay of $\text{Pb}(6^3\text{P}_0)$ in the presence of CH_3CHBr_2 . $[\text{PbEt}_4] = 4.3 \times 10^{14}$ molecules cm^{-3} ; $[\text{He}] = 1.1 \times 10^{18}$ atoms cm^{-3} ; $E = 141$ J. $[\text{CH}_3\text{CHBr}_2]$ (filter) = 3×10^{17} molecules cm^{-3} .

We were unable to measure with any reliability absolute rates for the removal of $\text{Pb}(6^3\text{P}_0)$ by the molecules HBr and Br_2 . Figure 7(a) shows the variation of k' with $[\text{HBr}]$; Fig. 7(b) shows the variation of $\ln\{\ln(I_0/I_{\text{tr}})\}$ ($t = 0$), which is directly related to $\ln[\text{Pb}(6^3\text{P}_0)]$ ($t = 0$), with $[\text{HBr}]$. Given the assumption of a linear relation between $[\text{PbEt}_4]$ ($t = 0$) and $[\text{Pb}(6^3\text{P}_0)]$ ($t = 0$) on photolysis, an assumption inherent in the empirical determination of γ [17], the data in Fig. 7(b) are a clear measure of the extent of direct reaction between PbEt_4 and HBr . We attribute the small increase in reaction rate k' with $[\text{HBr}]$ (Fig. 7(a)) as arising from the products of the direct reac-

TABLE 1

Absolute second order rate constants at 300 K for the reaction of $\text{Pb}(6^3\text{P}_0)$ with some Br-containing molecules

RBr	k_R ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
CH_3Br	$(3.7 \pm 0.5) \times 10^{-15}$
$\text{C}_2\text{H}_5\text{Br}$	$(5.0 \pm 0.5) \times 10^{-15}$
$\text{CH}_2\text{BrCH}_2\text{Br}$	$(5.3 \pm 0.3) \times 10^{-14}$
CH_2Br_2	$(1.4 \pm 0.2) \times 10^{-13}$
CH_3CHBr_2	$(6.0 \pm 0.5) \times 10^{-13}$
HBr	$< 10^{-15}$

tion referred to above and we report $k(\text{HBr})$ only as an upper limit. With Br_2 we were unable to measure decay rates for $\text{Pb}(6^3\text{P}_0)$ on account of rapid reaction between this halogen and the parent molecule, as evidenced in Fig. 8.

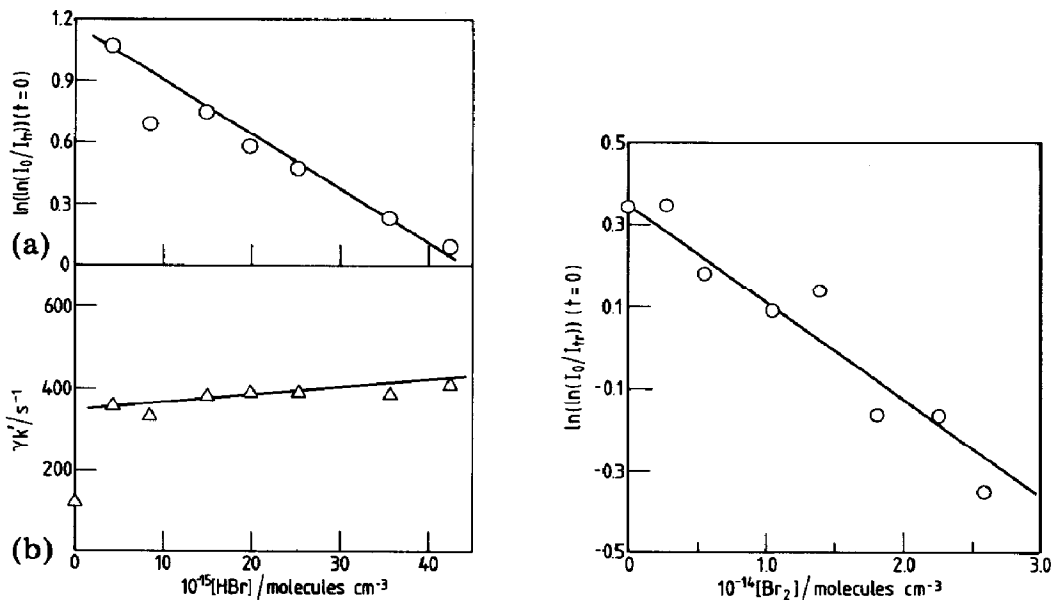
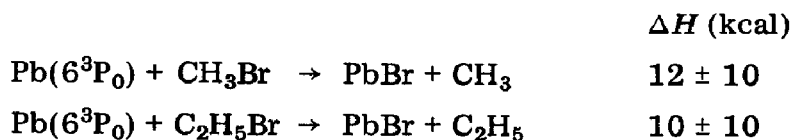


Fig. 7. (a) Variation of pseudo first order rate coefficient $\gamma k'$ for the decay of $\text{Pb}(6^3\text{P}_0)$ in the presence of HBr. (b) Variation of the initial yield of $\text{Pb}(6^3\text{P}_0)$ from the irradiation of PbEt_4 in the presence of HBr. $[\text{PbEt}_4] = 1.5 \times 10^{14} \text{ molecules cm}^{-3}$; $[\text{He}] = 1.1 \times 10^{18} \text{ atoms cm}^{-3}$; $E = 160 \text{ J}$; $[\text{HBr}]$ (filter) $= 3.0 \times 10^{18} \text{ molecules cm}^{-3}$.

Fig. 8. Variation of the initial yield of $\text{Pb}(6^3\text{P}_0)$ from the irradiation of PbEt_4 in the presence of Br_2 . $[\text{PbEt}_4] = 4.3 \times 10^{14} \text{ molecules cm}^{-3}$; $[\text{He}] = 1.1 \times 10^{18} \text{ atoms cm}^{-3}$; $E = 123 \text{ J}$; $[\text{Br}_2]$ (filter) $= 4.0 \times 10^{18} \text{ molecules cm}^{-3}$.

Figures 7(b) and 8 are important because they demonstrate the absence of any significant effect on the decay rates measured in the presence of alkyl bromides by any HBr or Br₂ formed on photolysis. In particular, there was no significant variation in $\ln\{\ln(I_0/I_{tr})\}(t=0)$ with the added alkyl bromides, indicating no direct reaction between PbEt₄ and RBr (or any of its photolysis products) on the time scales and with the low pressures involved here. Rapid reaction between lead alkyls and HBr and Br₂ is well established. We were unable to find an obvious alternative photochemical source of Pb(6³P₀) for the study of reaction with HBr and Br₂. Whilst we prepared the yellow oil of PbCl₄ from the reaction of ammonium hexachloroplumbate (NH₄)₂PbCl₆ with oleum [22], the PbCl₄ decomposed in the vapour phase when handled in a conventional vacuum system to yield solid PbCl₂.

Table 1 lists the absolute rate data obtained in this investigation. The rate data in Table 1 can be rationalized within the error limits of the appropriate thermochemical data. The magnitudes of the bond dissociation energies of all the relevant molecules, especially that for the diatomic molecule PbBr, are a matter of uncertainty. The error in $D(\text{PbBr})$ arises principally from the difficulty in interpreting predissociation in the spectrum of the molecule reported by Wieland and Newburgh [23]. Gaydon [24] and Barrow [25] are in agreement on the value of $D(\text{PbBr}) = 2.5 \pm 0.4$ eV arising from the analysis of Wieland and Newburgh's spectrum. Early compilations for $D(\text{CH}_3\text{—Br})$ and $D(\text{C}_2\text{H}_5\text{—Br})$ were essentially based on direct measurements of appearance potentials following electron impact [26 - 29] and favoured values, respectively, of 67 kcal and 65 kcal [30 - 32] (1 eV = 23.061 kcal mol⁻¹ [24]). More recent compilations, which appeal more to the extraction of rate data for fundamental reactions from mechanistic kinetics, favour higher values, namely $D(\text{CH}_3\text{—Br}) = 70.0 \pm 1.2$ kcal [33 - 35] and $D(\text{C}_2\text{H}_5\text{—Br}) = 67.8 \pm 1.5$ kcal [33 - 36]. If we attribute the departure of the magnitudes of the reaction rate constants for Pb(6³P₀) with CH₃Br and C₂H₅Br (Table 1) from the collisional number entirely to the effects of the energy barriers, these barriers would be of the order of 7 kcal. These are seen to be in accord with the thermochemistry of the following reactions, the errors for which are principally set by that for $D(\text{PbBr})$:



using the higher values for $D(\text{CH}_3\text{—Br})$ and $D(\text{C}_2\text{H}_5\text{—Br})$. The values for the C—Br bond energies for the other molecules listed in Table 1 are highly uncertain. One may estimate $D(\text{CH}_2\text{Br—Br})$ to be about 67 ± 5 kcal [33, 34]. Vedeneyev *et al.* [37] quote $D(\text{CH}_2\text{BrCH}_2\text{—Br}) = 66.8$ kcal, though the C—Br bond energies in their compilation in general appear to be high (*e.g.* $D(\text{CH}_3\text{—Br}) = 73.9$ kcal, $D(\text{C}_2\text{H}_5\text{—Br}) = 76.4$ kcal [37]) by comparison with those in the other compilations referred to above. We were unable to find any estimate for $D(\text{CH}_3\text{CHBr—Br})$ or for its free energy of formation (see later).

Finally we may note that the relationship between $\log_{10}k_R$ and the free energy of formation ΔG_f^0 of RBr (Hammett plot) for the molecules CH_3Br , $\text{C}_2\text{H}_5\text{Br}$, CH_2Br_2 and $\text{CH}_2\text{BrCH}_2\text{Br}$ [38] gives a good linear plot (Fig. 9). Whilst this plot only comprises data for four molecules, the error in the slope is only about 4% and at least demonstrates a consistent body of rate data.

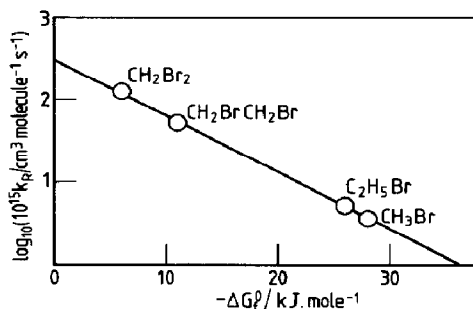


Fig. 9. Variation of the rate constant (k_R) for the reaction between $\text{Pb}(6^3\text{P}_0)$ and CH_3Br , $\text{C}_2\text{H}_5\text{Br}$, $\text{CH}_2\text{BrCH}_2\text{Br}$ and CH_2Br_2 , with their standard free energies of formation ΔG_f^0 .

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