Journal of Photochemistry, 2 (1973/74) 247–253

A KINETIC STUDY OF LEAD ATOMS, Pb(6^3P_0), BY ATOMIC ABSORPTION SPECTROSCOPY

D. HUSAIN and J. G. F. LITTLER

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

(Received May 15, 1973)

SUMMARY

A highly sensitive experimental method is described for the kinetic study of lead atoms in the lowest spin orbit component of the ground state configuration. Pb(6^3P_0) is generated by the pulsed irradiation of lead tetraethyl and monitored photoelectrically in absorption by time-resolved attenuation of atomic resonance radiation at $\lambda = 283.3$ nm $\{\mathrm{Pb}[7s(^3P^0_1) \rightarrow 6p^2(^3P_0)]\}$. In the presence of the gases He, CO, CO_2, N_2O, CH_4, C_2H_4 and C_2H_2, the decay of the ground state atom is slow and second order rate data are reported principally as upper limits for the absolute reaction rate constants. With the gases NO and O_2, overall third order kinetics are observed for the removal of Pb(6^3P_0), yielding the following third order rate constants:

	k(cm^6 molecule^{-2} s^{-1}, 300 K)
NO + He	$1.3 \pm 0.2 \times 10^{-31}$
NO + CO_2	$2.1 \pm 0.3 \times 10^{-30}$
O_2 + CO_2	$3.6 \pm 1.8 \times 10^{-32}$

Further, an estimate for the diffusion coefficient of the atom in helium is reported as $D_{\mathrm{Pb}(6^3P_0)-\mathrm{He}} \simeq 0.045$ cm^2 s^{-1} at one atmosphere.

INTRODUCTION

Whilst there has been only a relatively limited development in the direct kinetic study of heavy metal atoms in defined quantum states[1,2], it is nevertheless surprising that detailed rate data resulting from spectroscopic measurements on the 6^3P_J state of the lead atom have not been reported, despite its practical importance. Erhard and Norrish[3,4] have detected photographically all the J states of Pb($6^3P_{0,1,2}$) strongly in absorption, as well as the higher Pb(6^1D_2) state, during a kinetic spectroscopic study of the effect of lead tetraethyl on sensitized explosions of hydrocarbon–oxygen mixtures and its relevance to "knock" and "antiknock" in the internal combustion engine. The nature of the investigation did not permit collisional cross-sections for the reactions of any of these atomic states with molecules to be determined, as the system was one of variable high temperatures and we may reasonably assume that all the levels above the lowest 6^3P_0 level were populated according to the Boltzmann distribution. We have recently carried out detailed kinetic studies on $Pb(6^1D_2)$[5,6] and $Pb(6^1S_0)$[7,8], respectively 2.66 and 3.65 eV above the 6^3P_0 ground state[9]. These employed time-resolved atomic absorption spectroscopy following the pulsed irradiation of lead tetraethyl, and we have reported a large body of absolute rate data for the collisions of these atoms with various molecules. In the present paper, we describe the development and application of this method[5-8] of time-resolved attenuation of resonance radiation to the direct kinetic study of the lowest spin orbit component of the ground state of atomic lead, $Pb(6^3P_0)$, and report absolute kinetic data at room temperature.

EXPERIMENTAL

Details of the experimental arrangement for studying lead atoms in defined quantum states by time-resolved atomic absorption spectroscopy have been given hitherto[6] for the kinetic investigation of $Pb(6^1D_2)$. The general system employed here was similar. The lead atoms were generated by pulsed irradiation ($E = 562$ J, $\tau_{1/2} = \sim 25\ \mu s$) of lead tetraethyl in a coaxial lamp and vessel assembly[6,10], photolysis taking place below $\lambda = 235$ nm[11]. The atomic transition at $\lambda = 283.3$ nm $\{Pb[7s(^3P^0_1) \rightarrow 6p^2(^3P_0)]\}$[12], derived from a microwave-powered lamp (E.M.I. type 9776, E.M.I. cavity type C 111, incident power = 85 W), was attenuated subsequent to the photolysis flash. The attenuated emission was detected photoelectrically by means of a photomultiplier (E.M.I. 9781B) mounted on the exit slit of the monochromator (Spex Industries, Model 1650, "Minimate", blaze wavelength = 250.0 nm) employed for separation of the atomic line. The resulting photoelectric pulses, representing time-dependent atomic absorption at $\lambda = 283.3$ nm, were recorded in a transient recorder (Biomation model 610B) and expanded onto an XY recorder (Bryans Ltd.) for subsequent kinetic analysis.

Materials

$PbEt_4$, He, CO, NO, CO_2, N_2O, CH_4, C_2H_4 and C_2H_2 were prepared as described hitherto[6]. High purity O_2 (British Oxygen Co., Grade X) and N_2 (employed for the photolysis flash) (cylinder, "White Spot", BOC) were used directly.

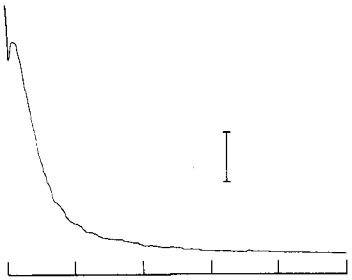
RESULTS AND DISCUSSION

Figure 1 shows a typical transient recorder trace for the production and decay of $Pb(6^3P_0)$ following the pulsed irradiation of lead tetraethyl in the presence of a large excess of helium buffer gas ($p_{\mathrm{He}}:p_{\mathrm{PbEt_4}} = \sim 5000:1$), ensuring no significant rise in temperature on photolysis. In the absence of a reactive added gas, the lifetime of this atomic state is clearly very long ($\sim$ 50–100 msec), being approximately one to two orders of magnitude greater than those of Pb(6^1D_2)[5,6] and Pb(6^1S_0)[7,8] which are also generated on photolysis. The lifetime of Pb(6^3P_0) is similarly greater than those of the higher spin orbit states, Pb(6^3P_1) and Pb(6^3P_2), which may also be detected on irradiation[13]. Thus, we may readily investigate the kinetic decay of Pb(6^3P_0) on a time scale by which relaxation from higher electronic states has been completed. Modification to the lifetime of the lead atom by the addition of various gases may be treated by employing the analysis of a single kinetic decay with appropriate consideration of the effect of these added gases on the lifetimes of Pb(6^1D_2) and Pb(6^1S_0)[5-8].

We have hitherto emphasized the nature of the experimental difficulties encountered when employing the modified Beer–Lambert law[14]:

$$I_{\mathrm{tr}} = I_0 \exp[-\varepsilon(\mathrm{cl})^{\gamma}] \qquad \text{(i)}$$

(where the symbols have their usual significance[14]) for the resonance transitions used to monitor the concentrations of Pb(6^1D_2)[6] and Pb(6^1S_0)[8]. Equation (i), when employed with the assumption of a proportionality between the initial concentration of the atomic state of lead and the initial concentration of the parent molecule ($\mathrm{PbEt_4}$), yields the result of a linear relation between $\ln[(\ln I_0/I_{\mathrm{tr}})]_{t=0}$ and $\ln(p_{\mathrm{PbEt_4}})$ ($t=0$), of slope γ[6,8,14]. As well as the normal problem of the sensitivity of the intercept of the first-order kinetic plot [$\ln(\ln I_0/I_{\mathrm{tr}})$ *vs.* t] to small



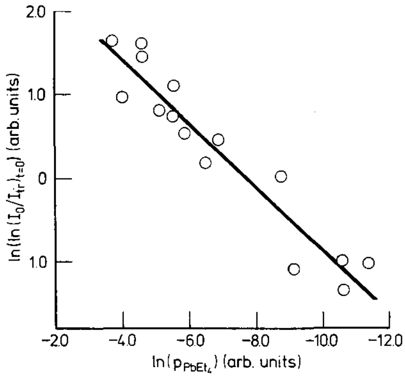


Fig. 1. A typical transient recorder trace for the decay of Pb(6^3P_0) obtained by monitoring the absorption of resonance radiation at λ = 283.3 nm {Pb[$7s(^3P^0_1)$ → $6p^2(^3P_0)$]} following the pulsed irradiation of lead tetraethyl. $p_{\mathrm{PbEt_4}} = 0.4\ \mathrm{N\ m^{-2}}$; $p_{\text{total with He}} = 3.3\ \mathrm{kN\ m^{-2}}$; $E = 562$ J. I = 20% absorption of light; time scale = 20 ms per division. (Leading edge = scattered light from photolysis pulse.)

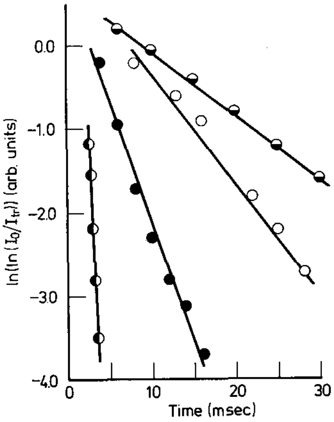
Fig. 2. Beer–Lambert plot for the absorption of resonance radiation by lead atoms at λ = 283.3 nm {Pb[$7s(^3P^0_1)$ → $6p^2(^3P_0)$]}. $p_{\text{total with He}} = 3.3\ \mathrm{kN\ m^{-2}}$.

deviations in the slope of this plot, and the difficulty in both measuring directly and handling $PbEt_4$ in the pressure range 0–1 N m^{-2} (1 Torr = 133 N m^{-2})[6,8], self-reversal in the spectroscopic lamp will clearly be more severe for transitions connecting with the ground state. We may therefore expect, from the general arguments of Braun and Carrington[15], large deviations from unity in the value of γ. Further, some departure in linearity when extrapolating the first-order plots to $t = 0$ will be expected on account of quenching to $Pb(6^3P_0)$ from higher states. The determination of γ constitutes one of the principal experimental difficulties of this work.

Figure 2 shows the plot for the measurement of γ for the resonance transition at $\lambda = 283.3$ nm. To construct this Figure, the decays of $Pb(6^3P_0)$ following the photolysis of different pressures of $PbEt_4$ in the presence of a fixed pressure of helium were investigated over a time range of up to 30 ms. The decays exhibited first-order kinetics. Indeed, qualitatively, the decay of the atom is far too rapid to be accounted for in terms of three body atomic recombination for the concentrations of lead atoms employed here[16], namely ~ 10^{-4}–10^{-5} Torr. Homer and Prothero[16] have shown that the rates of nucleation of lead in shock tube studies are satisfied by assuming recombination rates for lead atoms of the same order of magnitude as those exhibited for iodine atom recombination. Thus, second-order kinetic behaviour for $Pb(6^3P_0)$ is not expected in this system. Figure 2 contains data which result from various empirical procedures for extrapolating the first-order plots to $t = 0$. The slope of this graph yields $\gamma = 0.38 \pm 0.04$.

Kinetic data for Pb(6^3P_0)

The kinetic decay of $Pb(6^3P_0)$ will principally be determined by chemical processes and thus, in view of the weak bonds formed by lead atoms and the endothermicity of atomic abstraction reactions, rapid second-order kinetics at room temperature will not be expected. Therefore, we first present rate data for the removal of $Pb(6^3P_0)$ in which the overall decay of the atomic state is described by third order kinetics and is measureable. Figure 3 shows typical first-order plots for the decay of $Pb(6^3P_0)$ in the presence of nitric oxide with a fixed excess pressure of helium buffer gas. The slopes of the individual plots in Fig. 3 are given by $-\gamma k'$ where k' is the overall first order decay coefficient for $Pb(6^3P_0)$ and where γ has been determined as described. $\gamma k'$ shows a linear dependence on p_{NO} (Fig. 4) and a relatively weak dependence on the pressure of helium (Fig. 5). Third order kinetics were also observed for the decay of $Pb(6^3P_0)$ in the presence of NO and CO_2 (Fig. 5), with an enhanced rate constant, the decay rate in the presence of CO_2 alone being negligible (see later). The removal of $Pb(6^3P_0)$ in the presence of molecular oxygen was also found to exhibit third order kinetics, reaction to yield PbO being highly endothermic[17]. When the decay of $Pb(6^3P_0)$ exhibits third order kinetics, such as for its removal in the presence of NO + He, k' may be expressed in the form:



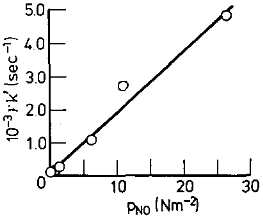


Fig. 3. First-order plots for the decay of Pb(6^3P_0) in the presence of nitric oxide. $p_{PbEt_4} = 0.23$ N m^{-2}; $p_{\text{total with He}} = 3.3$ kN m^{-2}; $E = 562$ J. p_{NO}(N m^{-2}): ⊖, 0.0; ○, 1.33; ●, 2.66; ◐, 11.7.

Fig. 4. Variation of the first-order rate coefficient (k') for the decay of Pb(6^3P_0) with the pressure of nitric oxide. $p_{PbEt_4} = 0.23$ N m^{-2}; $p_{\text{total with He}} = 3.3$ kN m^{-2}; $E = 562$ J.

$$k' = k_3[\text{NO}][\text{He}] + K \tag{ii}$$

k_3 is the third order rate constant and K represents a small contribution to the removal process by other processes and may be taken to be effectively constant in a series of kinetic runs. The resulting third order rate constants are presented in Table 1. Whilst the stability of PbO_2 is clear, we will not conjecture further on the possible species PbNO and comparisons one might make with analogous

TABLE 1

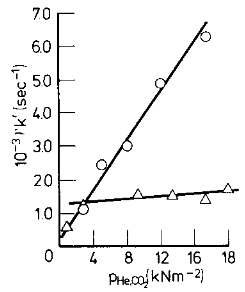
RATE DATA FOR Pb (6^3P_0)

Third-order rate constants (300 K) for the collisional removal of Pb(6^3P_0)

Collision partners	k(cm^6 molecule^{-2} s^{-1})
NO + He	$1.3 \pm 0.2 \times 10^{-31}$
NO + CO_2	$2.1 \pm 0.3 \times 10^{-30}$
O_2 + CO_2	$3.6 \pm 1.8 \times 10^{-32}$

Second-order rate data (300 K) for the collisional removal of Pb(6^3P_0)

Collision partner	k(cm^3 molecule^{-1} s^{-1})
He	$<10^{-16}$
CO	5×10^{-16}
CO_2	$0 \pm 2 \times 10^{-16}$
N_2O	$<1.8 \times 10^{-15}$
CH_4	$<10^{-16}$
C_2H_4	$1.4 \pm 0.2 \times 10^{-16}$
C_2H_2	$<10^{-16}$



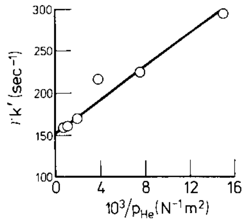


Fig. 5. Variation of the first-order rate coefficient (k') for the decay of $Pb(6^3P_0)$ in the presence of nitric oxide with total pressure. $p_{NO} = 6.7$ N m^{-2}; $E = 562$ J. △, He; ○, CO_2.

Fig. 6. Variation of the first-order rate coefficient (k') for the decay of $Pb(6^3P_0)$ with the reciprocal of the helium pressure. $p_{PbEt_4} = 0.27$ N m^{-2}; $E = 562$ J.

species from other Group IV elements such as that arising from the reaction of carbon atoms with nitric oxide. The mean lifetime of the initially produced PbNO* would lie in the range $\sim 10^{-11}$–10^{-10} s from the data in Table 1.

Table 1 also shows second order rate data for the removal of $Pb(6^3P_0)$ in the presence of various gases. All the rates are slow, including removal by N_2O where reaction to produce PbO would be highly exothermic[17], and the reported data are principally limits. The second order datum for helium is especially to be regarded as a crude limit as the decay rate for $Pb(6^3P_0)$ was found to decrease linearly with the reciprocal of the helium pressure. Approximating the rate of diffusion to be determined by a first order coefficient (β) given by the "long-time" solution of the diffusion equation of a cylinder $\{\beta \cong [(\pi^2/l^2) + (5.81/r^2)]\, D_{12}\}$[18], then the slope of the plot of k' *versus* $1/p_{He}$ (Fig. 6) yields D_{12}, the diffusion coefficient in helium. Thus we estimate $D_{Pb(6^3P_0)-He} \cong 0.045$ cm^2 s^{-1} at one atmosphere.

The appropriate thermochemistry indicates that many chemical reactions of $Pb(6^3P_0)$ will be characterized by large activation energies and we are therefore currently constructing a system in which it is proposed that attenuation of resonance radiation to this state be carried out at elevated temperatures in order to determine the Arrhenius parameters. Further, we are developing methods for monitoring $Pb(6^3P_1)$ and $Pb(6^3P_2)$ by attenuation of resonance radiation, in order to investigate spin orbit relaxation, but, clearly, chemical reactivity enhanced by the electronic energy may result in some cases. From a practical viewpoint, we may note that Homer and Hurle[19] have concluded that lead atoms have not hitherto been detected spectroscopically during an engine cycle on account of the low concentrations pertaining under the conditions ($\sim$ 10 parts in 10^6). The present development describes a method for monitoring lead atoms on a time-resolved basis, considerably more sensitive than other spectroscopic techniques employed hitherto. The method is capable of detection of lead atoms in the region of $\sim 10^{-6}$ Torr and is thus suited for application to the study of the atom during the Otto cycle for the purpose of investigating the mechanism of "anti-knock" behaviour exhibited by $PbEt_4$.

ACKNOWLEDGEMENTS

We thank Professor J. W. Linnett, F.R.S. for encouragement and laboratory facilities. We further thank the Associated Octel Company for financial assistance to one of us (J.G.F.L.).

REFERENCES

1 R. J. Donovan and D. Husain, *A. Rep. Chem. Soc.*, 68A (1971) 123.
2 R. J. Donovan, D. Husain and L. J. Kirsch, *A. Rep. Chem. Soc.*, 69A (1972) in press.
3 K. H. L. Erhard and R. G. W. Norrish, *Proc. Roy. Soc.*, A234 (1956) 178.
4 K. H. L. Erhard and R. G. W. Norrish, *Proc. Roy. Soc.*, A259 (1961) 297.
5 D. Husain and J. G. F. Littler, *Chem. Phys. Lett.*, 16 (1972) 145.
6 D. Husain and J. G. F. Littler, *J. C. S. Faraday Trans. II*, 68 (1972) 2110.
7 D. Husain and J. G. F. Littler, *J. Photochem.*, 1 (1972) 327.
8 D. Husain and J. G. F. Littler, *J.C.S. Faraday Trans. II*, 69 (1973) 842.
9 C. E. Moore (ed.), Nat. Bur. Stand., Circular 467, *Atomic Energy Levels*, Vols. I–III, U.S. Government Printing Office, Washington D.C., 1958.
10 P. P. Sorokin, J. R. Lankard, V. C. Moruzzi and E. C. Hammond, *J. Chem. Phys.*, 48 (1968) 4726.
11 A. B. F. Duncan and J. W. Murray, *J. Chem. Phys.*, 2 (1934) 636.
12 C. H. Corliss and W. R. Bozman, Experimental transition probabilities of spectral lines of seventy elements, *Nat. Bur. Stand. Monogr. 53*, U.S. Government Printing Office, Washington, D.C. (1962).
13 D. Husain and J. G. F. Littler, unpublished results.
14 R. J. Donovan, D. Husain and L. J. Kirsch, *Trans. Faraday Soc.*, 66 (1970) 2551.
15 W. Braun and T. Carrington, *J. Quant. Spectros. Rad. Trans.*, 9 (1969) 133.
16 J. B. Homer and A. Prothero, *J.C.S. Faraday Trans. I*, 69 (1973) 673.
17 J. Drowart, R. Colin and G. Exsteen, *Trans. Faraday Soc.*, 61 (1965) 1376.
18 A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms*, Cambridge University Press, London, 1934, p. 247; M. W. Zemansky, *Phys. Rev.*, 34 (1929) 213.
19 J. R. Homer and I. R. Hurle, *Proc. Roy. Soc.*, A327 (1972) 61.