A KINETIC STUDY OF THE THIRD ORDER REACTIONS OF ATOMIC LEAD: $Pb(6^3P_0) + O_2 + M$ AND $Pb + NO + M$

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Summary

The third order kinetic reactions $Pb + O_2 + M$ (reaction (1)) and $Pb + NO + M$ (reaction (2)) have been studied by atomic absorption spectroscopy of $Pb(6^3P_0)$ following flash photolysis. $Pb(6^3P_0)$ was generated by pulsed irradiation of $PbEt_4$ in the presence of excess buffer gas (M) and was monitored photoelectrically in absorption in the single shot mode by time resolved attenuation of atomic resonance radiation at $\lambda = 283.3$ nm due to the transition $Pb(7s(^3P_1^0)) \leftarrow Pb(6p^2(^3P_0))$. Absolute third order rate constants are reported for reaction (1) for the gases He, N_2, CO, CO_2, CH_4, CF_4, SF_6, C_2H_6, C_2H_2 and C_2H_4. A similar study is also presented for reaction (2) which is usually of the order of 50 - 100 times faster than reaction (1) for a given third body M. On this account, reaction (2) is found to be highly sensitive to impurities of O_2 and a number of the analogous rate constants are less reliable. The rate data are discussed with reference to other atom—molecule recombination processes, to atomic recombination and to the quenching of atomic fluorescence.

Introduction

A systematic study of the reactions of heavy metal atoms in specific electronic states is developing, partly motivated by an interest in the relationship between electronic structure and reactivity [1 - 3]. There is further a current interest in the reactions of the ground atomic states which can be seen as complementary to excited atom studies [1 - 3] and falling within the overall fundamental framework of the collisional behaviour of atomic species in these defined states. A focal point of such studies is clearly seen from investigations on group V atoms, including $P(3^4S_{3/2})$ [4], $Sb(5^4S_{3/2})$ [5] and $Bi(6^4S_{3/2})$ [6]. In contrast, as part of the programme aimed at characterising the kinetic processes of all states of group IV atoms arising from the np^2 configuration ($^3P_{0,1,2}$, $^1D_2$, $^1S_0$), some rate data have been

reported for the ground state species $C(2^3P_J)$ [7, 8], $Ge(4^3P_0)$ [9, 10], $Sn(5^3P_0)$ [11, 12] and $Pb(6^3P_0)$ [13, 14].

An interesting class of third order reactions of heavy atoms (X) that have emerged are those of $X + O_2 + M$ and, in some cases, $X + NO + M$ (M is third body). Both groups of reactions have been reported in preliminary studies of $Pb(6^3P_0)$ [13, 14] and, recently, the reactions of $Sb + O_2 + M$ [5] and $Bi + O_2 + M$ [6] have been described in detail. In this paper we report a detailed investigation of $Pb + O_2 + M$ and $Pb + NO + M$, employing a considerably superior experimental system to that described hitherto for time resolved absorption spectroscopy used to monitor $Pb(6^3P_0)$ [13] and involving a wide range of third bodies M. Such rate processes are clearly of importance in the internal combustion engine operating with lead additives and in exhaust gases, as well as being of fundamental interest *per se*. The resulting rate data are discussed by analogy with other atom–molecule recombination processes, atomic recombination and quenching of atomic fluorescence.

Experimental

Whilst this investigation employed monitoring of $Pb(6^3P_0)$ by time resolved attenuation of the atomic resonance radiation at $\lambda = 283.3$ nm due to the transition $Pb(7s(^3P_1^0) \leftarrow 6p^2(^3P_0))$ following pulsed irradiation of lead tetraethyl, a new experimental arrangement was constructed for the present study, which was different in a number of major respects to that used in the preliminary studies [13]. A block diagram of the apparatus is shown in Fig. 1. The coaxial reactor and vessel assembly was similar to that
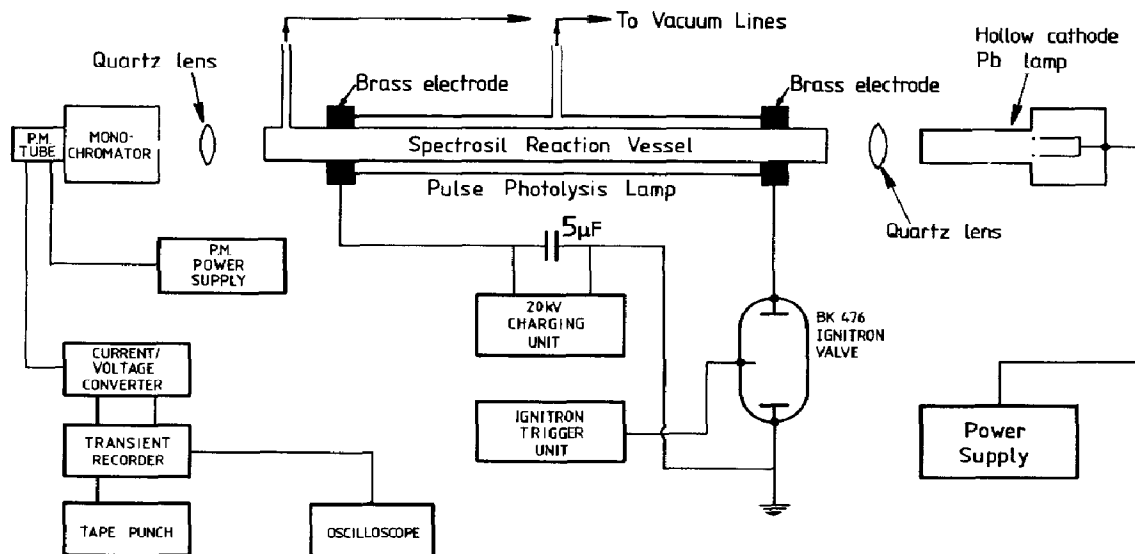

Fig. 1. A block diagram of the apparatus for the kinetic study of $Pb(6^3P_0)$ by time resolved attenuation of atomic resonance radiation.

reported earlier [13] but the overall system differed in most other major respects.

Spectroscopic source

It is a general experience that microwave powered atomic emission sources, be they flow sources of the type employing a Fehsenfeld cavity [15] as used, for example, in time resolved studies of $Bi(6^4S_{3/2})$ [6] or sealed microwave powered sources of the type described in the earlier investigation of $Pb(6^3P_0)$ [13] (EMI electrodeless discharge tube, EMI Cavity C 111), are usually considerably more intense than standard hollow cathode sources. Unlike routine steady state analytical investigations using commercial atomic absorption spectrophotometers which employ chopping of radiation coupled with phase sensitive detection, time resolved resonance absorption measurements, especially in the "single shot" mode, require a high spectroscopic incident intensity I_0 in order to achieve a suitable signal to noise ratio. Mechanically constructed high current hollow cathode sources operating with an inert gas flow (Glomax hollow cathode lamp, Barnes Engineering, U.S.A.) have been successfully employed in, for example, the kinetic study of $Pb(6^3P_{1,2})$ by Ewing *et al.* [16]. A new spectroscopic source that was different from that employed previously [13] for the resonance transition at $\lambda = 283.3$ nm was sought firstly because this transition is relatively weak when derived from a sealed microwave powered source compared with those connecting with other states arising from the $6p^2$ configuration ($6^3P_{1,2}$, 6^1D_2, 6^1S_0 [17 - 19]) despite the reasonably high Einstein coefficient for the transition ($\lambda = 283.3$ nm, $gA = 1.8 \times 10^8$ s^{-1} [20]). Secondly, commercial sealed microwave powered atomic emission sources vary considerably in both stability and operating lifetime, as found with the Pb source. Thirdly, we found that even a microwave powered flow lamp employing various $PbEt_4$–He mixtures with a Fehsenfeld cavity [15] would not yield the required combination of stability and intensity at $\lambda = 283.3$ nm.

It was a surprise to discover that the intensity of the $\lambda = 283.3$ nm transition obtained from a quartz constructed "high spectral output" Pb hollow cathode lamp (Westinghouse, U.S.A.) operating at a relatively low current (1000 V, 7 mA), compared with those employed with water cooled mechanically constructed hollow cathode lamps (*e.g.* Glomax, Barnes Engineering, current up to 1000 mA), was considerably superior at this particular wavelength to the intensity from a microwave powered source. A hollow cathode source of the present type also has, of course, the advantages accompanying stability. Figure 2(A) shows a portion of the atomic spectrum of lead in the region of the $\lambda = 283.3$ nm resonance transition taken on a relatively high resolution monochromator. Figure 2(B) shows the same spectrum taken on the low resolution monochromator employed in the kinetic investigation under slit width conditions actually used in the pulsed experiments. The $\lambda = 282.3$ nm transition ($6d(^3D_2^0) \rightarrow 6p^2(^3P_2)$) is seen not to be resolved. However, oscilloscope monitoring of the d.c. level for the $\lambda = 283.3$ nm transition of $Pb(6^3P_0)$ shows that this line is suitably resolved and can be employed for kinetic measurements.
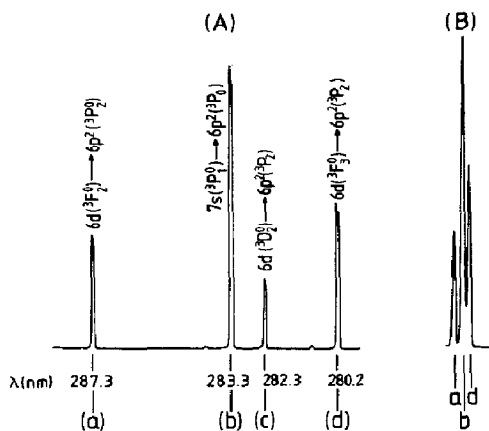
Fig. 2. A portion of the atomic spectrum of Pb from the "high spectral output" hollow cathode lamp: (A) Hilger and Watts "Monospek" 1000 monochromator: slit widths, 0.03 mm; hollow cathode lamp voltage, 1110 V (7 mA). (B) Limited resolution spectrum (Grubb Parsons "M2" monochromator): slit widths, 0.25 mm; hollow cathode lamp voltage, 750 V (7 mA).

Data handling

After the low energy pulsed irradiation (E = 250 J) of $PbEt_4$ in the presence of excess buffer gas M to ensure no significant temperature rise on photolysis ($p(M)$: $p(PbEt_4)$ was typically 30 000:1), the transient $Pb(6^3P_0)$ atoms were monitored photoelectrically in absorption by means of the λ = 283.3 nm resonance transition. As hitherto [13], resonance absorption was detected by means of an EMI 9783B photomultiplier mounted, in this case, on the exit slit of a grating monochromator of limited resolution (Grubb Parsons, model M2, see Fig. 2) which was somewhat superior in resolution to the smaller instrument employed previously [13].

By contrast with the earlier procedure in which the photoelectric signals were stored in a transient recorder and were analysed in analogue form following transference to an XY recorder, the absorption signals here were digitised and analysed by means of the university's computer (IBM 370). The photoelectric signals were thus amplified by means of a current to voltage converter employing a fast-settling operational amplifier [21] and then transferred to a transient recorder (Data Laboratories Model DL 905). The signals were digitised, stored and punched onto paper tape in ASCII code (Datadynamics punch 1133) for subsequent analysis in the IBM 370 machine.

We employ here the modified Beer–Lambert law [22]:

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

(where the symbols have their usual significance [22]) and take the previously determined value of γ = 0.38 ± 0.04 [13] for the λ = 283.3 nm transition. This is clearly an approximation as the emission lineshapes from the hollow

cathode lamp and the sealed microwave powered source used previously [13] will not be identical. Calculation of the rate constants from the observed data depends upon the reciprocal of γ (see later) and any variation from the above value for this quantity will be reflected accordingly in the absolute rate data. Given especially the wide variations in the total pressures with different gases in these experiments with the accompanying effects on Lorentz broadening and the enormity of calibrating γ for each total pressure for each third body M, we feel that the constant value given above is a sensible approximation.

We have given lengthy consideration to the modified Beer–Lambert law (eqn. (I)) in logarithmic form for atoms which are and are not characterised by nuclear hyperfine splitting (NHFS) [4 - 6, 10, 23]. The conclusion of these considerations, particularly in terms of the "curves of growth" [24], is that there are large ranges of particle density over which γ in eqn. (I) can be taken as sensibly constant for the two cases, *i.e.* with and without NHFS. Pb is characterised by four isotopes, ^{204,206,207,208}Pb, of which only ^{207}Pb (21.11%) has a nuclear spin ($I = \frac{1}{2}$) [25] and will therefore give rise to a nuclear magnetic dipole interaction. Employing the simple vector model for nuclear hyperfine interaction and the standard selection rules, $\Delta F = 0, \pm 1$ [26], the ^{207}Pb isotope will split the $7s(^{3}P_1^0)$–$6p^2(^{3}P_0)$ transition into two lines, a case presented in terms of the "curve of growth" for the P atom ($I = \frac{1}{2}$) in some detail by Husain and Norris [4]. Further, the curve of growth calculations [4] are seen to be relatively insensitive to Lorentz broadening at the pressures employed here, giving further justification to the use of a constant γ factor.

A kinetic detail which merits note concerns the determination of the unattenuated intensity I_0. In order to avoid extending the complete decay signal of I_{tr} to infinite time, use is made of the two time bases in the transient recorder as described hitherto for the study of $Bi(6^4S_{3/2})$ [6]. The decay trace was divided into two regions: (1) 824 points of the 1024 point memory were recorded for analysis of the transient signal; (2) the remaining 200 points were recorded over 1 s to measure the I_0 value individually for each trace.

Materials

Particular care was taken in the preparation of materials, especially those to be employed at high pressures as third bodies, with regard to degassing and the removal of residual traces of O_2 by freeze–pump–thaw cycles. This is seen later to be particularly important in experiments involving low pressures of NO. Apart from paying special attention to the procedures for degassing and fractional distillation, we do not feel that a detailed description for preparing standard materials is justified beyond reference to previous publications (PbEt$_4$, He, Kr (for the pulse photolysis lamp), N$_2$, O$_2$, CO, NO, CO$_2$, CH$_4$, SF$_6$, C$_2$H$_6$, C$_2$H$_4$ and C$_2$H$_2$ [18, 27]).
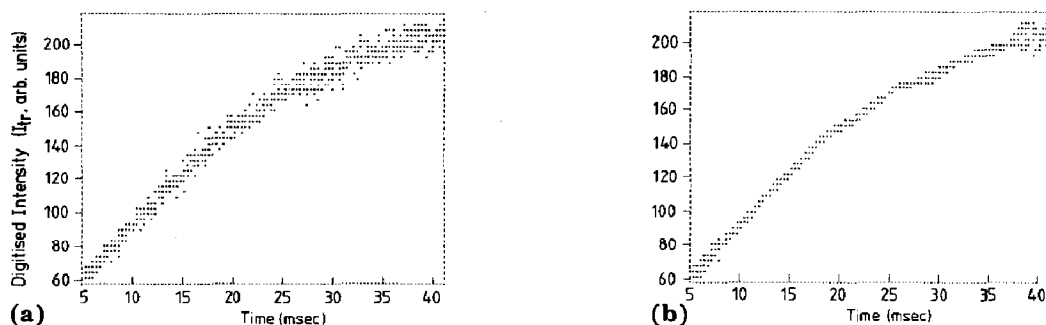
Fig. 3. Digitised time variation of the transmitted light intensity at λ = 283.3 nm for the transition $Pb(7s(^3P_1^0)) \rightarrow Pb(6p^2(^3P_0))$, indicating the decay of resonance absorption by ground state lead atoms: $p(PbEt_4)$ = 0.10 N m^{-2}; p(total with SF_6) = 2.66 kN m^{-2}; E = 250 J; (a) unsmoothed data; (b) smoothed data.

Results and discussion

Figure 3(a) shows a typical example of the computerised output of the digitised time variation of the transmitted light intensity at λ = 283.3 nm, indicating the decay of resonance absorption by $Pb(6^3P_0)$ after the pulsed irradiation of low pressures of $PbEt_4$. As this investigation is concerned with the effect of various inert third bodies on the kinetic decay of ground state lead atoms (in the presence of O_2 and NO), we present here SF_6 as an example of the added buffer gas. We employ the numerical data smoothing procedure of Savitsky and Golay [28] in order to make optimum use of the data, particularly at low degrees of light absorption. Figure 3(b) shows the computerised output of the smoothed data of Fig. 3(a). Two aspects of the decay may immediately be noted. Firstly, the lifetime of $Pb(6^3P_0)$ is clearly seen to be long by the standards of time resolved experiments. Secondly, in this instance, the kinetic analysis has been delayed by 5 ms. This is necessitated as a result of the role played by the higher lying spin orbit state $Pb(6^3P_1)$ ($\Delta E\ ^3P_{1-0}$ = 0.969 eV [29]) in this system, a role which is more prominent in the presence of O_2 and which requires detailed consideration before proceeding with the kinetic analysis.

It is difficult in pulsed irradiation experiments to generate $Pb(6^3P_0)$ photochemically from $PbEt_4$ in quantities sufficient for effective monitoring in the "single-shot" mode and to avoid producing simultaneously $Pb(6^3P_1)$. It is established from a detailed kinetic analysis [11] that a rapid near resonant electronic energy exchange process takes place in the presence of O_2:

$$Pb(6^3P_1) + O_2(X^3\Sigma_g^-) \rightleftharpoons Pb(6^3P_0) + O_2(a^1\Delta_g)$$

$$\Delta E = +99\ cm^{-1}\ [29, 30]$$
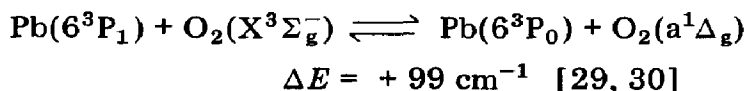
This analysis is fully consistent with various limiting rates for the decay of $Pb(6^3P_0)$ and $Pb(6^3P_1)$ at both high and low pressures of O_2 and of added quenching gas Q, in this case the third body M [11, 13, 17]. Similar be-
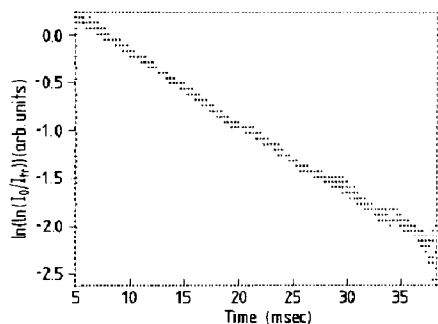
Fig. 4. Typical pseudo first order plot for the decay of $Pb(6^3P_0)$ obtained by monitoring the absorption of light at $\lambda = 283.3$ nm due to the transition $Pb(7s(^3P_1^0)) \leftarrow Pb(6p^2(^3P_0))$: $p(PbEt_4) = 0.10$ N m^{-2}; p(total with SF_6) = 2.66 kN m^{-2}; $E = 250$ J.

haviour has been found for $Tl(6^2P_{3/2}) + O_2$ [31], and in the case of $I(5^2P_{1/2}) + O_2$ the rapid establishment of an equilibrium has been directly demonstrated by spectroscopic observation of both $I(5^2P_{1/2})$ and $O_2(a^1\Delta_g)$ [32]. In this investigation complication to the kinetic analysis for $Pb(6^3P_0)$ is aggravated by the high collisional metastability of $O_2(a^1\Delta_g)$ [2, 3]. This is manifest by the observation of a growth component in the overall decay of $Pb(6^3P_0)$ which is removed essentially following the relaxation of $Pb(6^3P_1)$. In general, small traces of acetylene were added (typically $p(C_2H_2) = 4.0$ N m^{-2}) which effectively quench $Pb(6^3P_1)$ within a time scale that is short by comparison with those of the present investigation ($k\{Pb(6^3P_1) + C_2H_2\} = (3.5 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) [17]. This does not significantly affect the kinetics of $Pb(6^3P_0)$ ($k\{Pb(6^3P_0) + C_2H_2\} < 10^{-16}$ cm^3 molecule^{-1} s^{-1} [13]) but merely facilitates the overall electronic relaxation. Hence, whilst we record the complete trace, we employ a delay before analysing kinetically the decay of the ground state atom. By the same token, some curvature in the appropriate plots ($\gamma k'$ versus $p(O_2)$, see later) may be obtained in the variation of the overall decay of $Pb(6^3P_0)$ at low pressures of O_2. Thus, measurements are taken at higher pressures of both the molecular oxygen and third body concentrations.

Figure 4 shows the computerised form of the first order plot for $Pb(6^3P_0)$ from the data of Fig. 3(b) following eqn. (I), the slope of which is given by $-\gamma k'$ where k' is the overall first order decay coefficient. Figures 5 and 6 show the linear dependence of k' ($\gamma k'$) on $p(O_2)$ and $p(SF_6)$, respectively. Similar behaviour was observed for the decay of $Pb(6^3P_0)$ in the presence of O_2 and other third bodies. Hence k' can be expressed in the form

$$k' = K + k_3^M[O_2][M] \tag{II}$$

where K represents the removal of $Pb(6^3P_0)$ by processes other than

$$Pb(6^3P_0) + O_2 + M \xrightarrow{k_3^M} \text{products} \tag{1}$$

This is taken to be a constant in a series of kinetic runs in which $[O_2]$ and
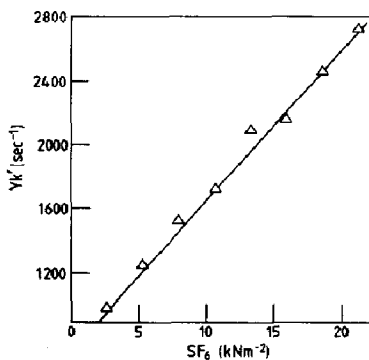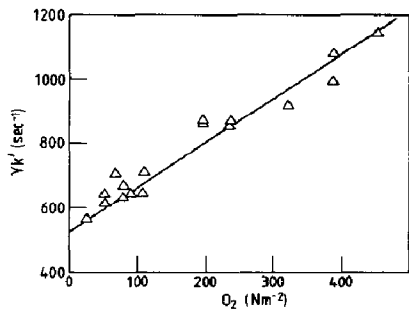
Fig. 5. Pseudo first order rate coefficients $\gamma k'$ for the decay of $Pb(6^3P_0)$ in the presence of oxygen (third body SF_6): $p(PbEt_4) = 0.08$ N m^{-2}; p(total with SF_6) = 2.66 kN m^{-2}; $E = 250$ J.

Fig. 6. Pseudo first order rate coefficients $\gamma k'$ for the decay of $Pb(6^3P_0)$ in the presence of O_2 and SF_6: $p(PbEt_4) = 0.08$ N m^{-2}; $p(O_2) = 200$ N m^{-2}; $E = 250$ J.
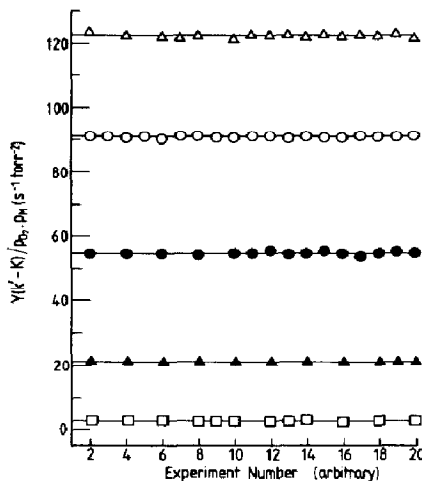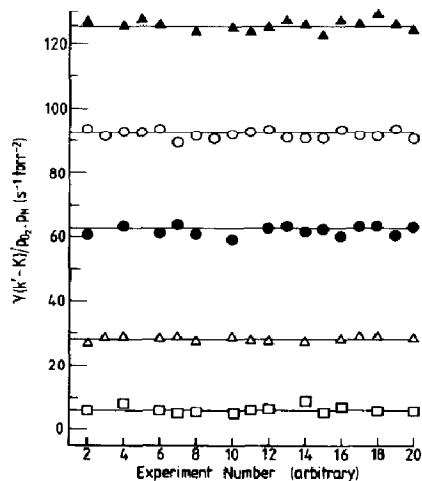
Fig. 7. Third order rate data for $Pb + O_2 + M$ $\gamma(k' - K)/p(O_2)p(M)$ (s^{-1} Torr^{-2}). Shifts of data for various M were: $\square$ He, 0.0; $\triangle$ SF_6, + 20; $\bullet$ CO_2, + 50; $\circ$ N_2, + 80; $\blacktriangle$ CF_4, + 110.

Fig. 8. Third order rate data for $Pb + O_2 + M$ $\gamma(k' - K)/p(O_2)p(M)$ (s^{-1} Torr^{-2}). The scaling of data for various M (where $\gamma(k' - K)/p(O_2)p(M) = \alpha$) was: $\square$ CO, 10^{-1} α + 20; $\blacktriangle$ CH_4, 10^{-2} α + 20; $\bullet$ C_2H_2, 10^{-2} α + 50; $\circ$ C_2H_6, 10^{-3} α + 90; $\triangle$ C_2H_4, 10^{-5} α + 120.

[M] are varied. Variations in K will arise from one batch of experiments to another on account of differences in dispensing low pressures of $PbEt_4$. The effect of such a variation can be readily compensated for by comparing all first order rate coefficients k' with that of a blank $(K, p(O_2) = 0)$. The absolute third order rate constant for the reaction is then simply given by

$$k_3^M = \gamma(k' - K)/p(O_2)p(M)\gamma \tag{III}$$

using the above value for γ. The data for the gases investigated here are presented in Figs. 7 and 8 in a graphical form commensurate with eqn. (III). The results for k_3^M are presented in Table 1.

TABLE 1

Third order rate constants (k_3^M, cm^6 molecule^{-2} s^{-1}, 300 K) for the collisional removal of $Pb(6^3P_0)$ by O_2 in the presence of various third bodies M

M	k_3^M
He	$1.4 \pm 0.5 \times 10^{-32}$
N_2	$3.2 \pm 0.5 \times 10^{-32}$
CO	$6.5 \pm 0.7 \times 10^{-32}$
CO_2	$3.2 \pm 0.5 \times 10^{-32}$
	$3.6 \pm 1.8 \times 10^{-32}$ [13]
CH_4	$3.1 \pm 0.5 \times 10^{-31}$
CF_4	$3.9 \pm 0.3 \times 10^{-32}$
SF_6	$2.1 \pm 0.1 \times 10^{-32}$
C_2H_6	$2.7 \pm 0.5 \times 10^{-30}$
C_2H_2	$1.2 \pm 0.1 \times 10^{-30}$
C_2H_4	$5.8 \pm 1.0 \times 10^{-28}$

The decay of $Pb(6^3P_0)$ in the presence of NO generally exhibited third order kinetics similar to those described for $Pb + O_2 + M$; however, the kinetic data were often not consistent, we believe on account of trace impurities of O_2 in the third bodies M employed at high pressures. $Pb(6^3P_0)$, of course, exhibited good first order kinetics in all experiments with NO, similar to those shown in Fig. 4. Figures 9 and 10 show the linear dependence of k' ($\gamma k'$) on $p(NO)$ and $p(CO_2)$ respectively. Similar pairs of plots were obtained for the majority of third bodies. Figure 11 shows graphically the values for the absolute rate constants for

$$Pb(6^3P_0) + NO + M \xrightarrow{k_3^M} \text{products} \qquad (2)$$

in the form of $\gamma(k' - K)/p(NO) \, p(M)$ for M = CO_2 and SF_6. With the gases He, N_2, CH_4 and CF_4, the following behaviour was observed: k' showed a clear linear dependence on both $p(NO)$ and $p(M)$; however, the value of k_3^M calculated from the plot of $\gamma k'$ versus $p(NO)$ (fixed [M]) was generally a variable factor of about 2 greater than that obtained from the plot of $\gamma k'$ versus $p(M)$ (fixed [NO]). The overall third order kinetic dependence is clear. It can be seen that the rates for $Pb + NO + M$ are a factor of about 10^2 times greater than those for $Pb + O_2 + M$, limiting the pressure range of NO that can be employed in the experiments. The kinetic data for $Pb + NO + M$ can be sensibly explained if we consider O_2 as an impurity in the high pressures of the third body M at a typical level of about 100 ppm, causing partial removal of the low pressures of NO. In these cases we have taken the value of k_3^M from the slopes of $\gamma k'$ versus $p(NO)$ (fixed [M]) and the resulting rate constants may be considered as correct to within a factor of about 2. For the gases CO and C_2H_6 the dependences of $\gamma k'$ on $p(M)$
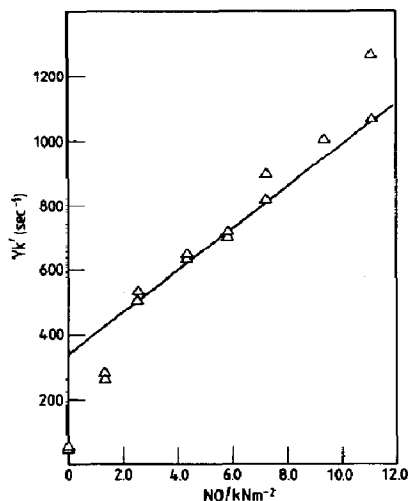
Fig. 9. Pseudo first order rate coefficients $\gamma k'$ for the decay of $Pb(6^3P_0)$ in the presence of nitric oxide (third body CO_2): $p(PbEt_4) = 0.09$ N m^{-2}, p(total with CO_2) = 2.66 kN m^{-2}; $E = 250$ J.
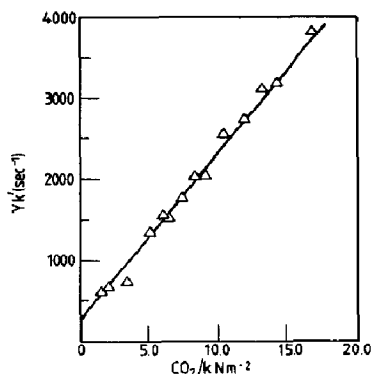
Fig. 10. Pseudo first order rate coefficients $\gamma k'$ for the decay of $Pb(6^3P_0)$ in the presence of NO and CO_2: $p(PbEt_4) = 0.09$ N m^{-2}, $p(NO) = 5.3$ N m^{-2}; $E = 250$ J.
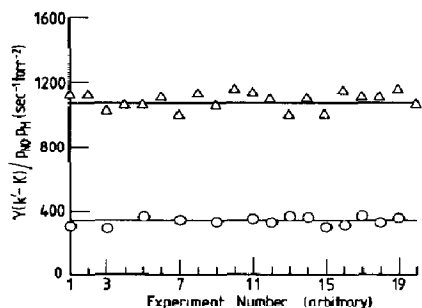
Fig. 11. Third order rate data $\gamma(k' - K)/p(NO)\,p(M)$ (s^{-1} Torr^{-2}) for Pb + NO + M (M = CO_2, SF_6): $\circ$ SF_6; $\triangle$ CO_2, + 400.

were very weak, and the quoted values for k_3^M given in Table 2 from the plots of $\gamma k'$ *versus* $p(NO)$ (fixed [M]) should be viewed with caution. No rates are reported for C_2H_2 and C_2H_4 where there was clearly chemistry between all the reactants following photolysis as judged by the yields and decays of $Pb(6^3P_0)$.

There have, of course, been many investigations concerned with atom—molecule recombination rates for overall processes such as H + O_2 + M and O + O_2 + M but, as expected, the measurements have not generally been concerned with the wide variation of the third body M presented in this study [33]. A particularly significant fundamental contribution, in our opinion, is that of Clyne *et al.* [34] who consider the rates of atom (O, H) + diatomic molecule + Ar (*i.e.* fixed M) and show, at least qualitatively, that the rates increase with the density of energy levels in the newly formed molecule.

TABLE 2

Third order rate constants ($k_{3'}^M$, cm^6 molecule^{-2} s^{-1}, 300 K) for the collisional removal of Pb(6^3P_0) by NO in the presence of various third bodies M

| M	$k_{3'}^M$
CO_2	$1.7 \pm 0.3 \times 10^{-30}$
	$2.1 \pm 0.3 \times 10^{-30}$ [13]
SF_6	$8.7 \pm 1.3 \times 10^{-31}$
He	$\sim 2.0 \times 10^{-30}$ [a]
	$\sim 2.6 \times 10^{-30}$ [b] [13]
N_2	$1.2 \pm 0.2 \times 10^{-30}$ [a]
CH_4	$7.1 \pm 0.2 \times 10^{-31}$ [a]
CF_4	$3.1 \pm 1.1 \times 10^{-30}$ [a]
CO	$(2.6 \pm 0.2 \times 10^{-31})$[c]
C_2H_6	$(1.0 \pm 0.2 \times 10^{-30})$[c]

[a] Correct to within a factor of about 2, see Discussion.
[b] Recalculated from data of ref. 13.
[c] Third order kinetics assumed, see Discussion.

An obvious comparison with the present rate data, which presumably reflect energy transfer efficiencies of the initially formed PbO_2^* and PbNO* by the various third bodies, would be to consider relative third order recombination rates for I + I + M. Where a comparison can be made with the third bodies employed here [35] there is a rough trend between the two sets of rate data; however, the correlation is not a strong one. Nevertheless, this absence of a strong correlation is hardly surprising in view of the operation of two mechanisms for atomic recombination: an "energy transfer" mechanism for species such as noble gases and N_2 and a "radical complex" mechanism for large molecules where the species M–I is characterised by a significant thermodynamic stability [36]. The observation of third order kinetics in these experiments clearly does not differentiate between the two recombination mechanisms. On the other hand, the high relative efficiencies shown by the unsaturated molecules, C_2H_2 and C_2H_4 (and also C_2H_6), for Pb + O_2 (Table 1) may reflect the role of an intermediate of the type

$$\begin{array}{c} Pb \\ / \backslash \\ -HC \!-\!\!-\! CH- \end{array}$$
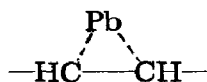
Further consideration of this aspect of the results would be speculative.

Perhaps the least satisfactory comparison for the present rate data, though one which may at least be noted, is that with electronic energy transfer data such as, for example, with fluorescence quenching rates for, say, Hg(6^3P_1) for which a wide range of collisional deactivators have been investigated [37]. Again, there is an approximate trend between the two sets of

data but there are serious anomalies such as for CF_4 (and, by general experience, He). This is to be expected as, apart from special effects for those molecules which cause efficient spin orbit relaxation for $Hg(6^3P_{1 \to 0})$ [38, 39], quenching of the fluorescing state, in this case $Hg(6^3P_1)$, involves the transfer of large quantities of electronic energy. By contrast, third order recombination efficiencies indicate energy transfer from the newly formed vibrationally excited molecule to within a few RT of the dissociation limit.

Acknowledgments

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