THE REACTION OF GROUND STATE LEAD ATOMS, Pb(6 ^{3}P$_0$), WITH CH$_3$Cl, C$_2$H$_5$Cl, n-C$_3$H$_7$Cl AND SF$_6$ AT ELEVATED TEMPERATURES BY TIME-RESOLVED ATOMIC RESONANCE ABSORPTION SPECTROSCOPY

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Summary

The reactions of ground state lead atoms, Pb(6 ^{3}P$_0$), with the molecules CH$_3$Cl, C$_2$H$_5$Cl, n-C$_3$H$_7$Cl and SF$_6$ have been studied over the range of elevated temperatures 594 - 819 K by time-resolved atomic resonance absorption spectroscopy. Pb(6 ^{3}P$_0$) was generated by the low energy flash photolysis of PbBr$_2$ vapour and monitored photoelectrically in the "single-shot mode" at $\lambda = 283.3$ nm (Pb(7s(^{3}P$_1^o$)) $\leftarrow$ Pb(6p^2(^{3}P$_0$))), on a time scale long by comparison with that for the relaxation of Pb(6p^2(^{3}P$_{1,2}$)). The decay profiles of the ground state lead atoms were characterized in the presence of the halides RX, leading to the determination of the absolute second-order rate constants k_{RX} for removal and the following Arrhenius parameters ($k_{RX} = A \exp(-E/RT)$):

RX	A ($\times 10^{-11}$ cm^3 molecule^{-1} s^{-1})	E (kJ mol^{-1})
CH$_3$Cl	4.5	74.2 ± 3.8
C$_2$H$_5$Cl	8.0	76.2 ± 8.4
n-C$_3$H$_7$Cl	7.2	65.8 ± 3.5
SF$_6$	74	93.0 ± 7.3

(errors, 1σ). These data are considered in the context of the relevant thermochemistry and compared with the analogous results for the reactions of lead atoms with alkyl bromides that we have reported previously. These two groups of measurements constitute the first body of Arrhenius data for halogen atom abstraction from alkyl halides by lead atoms, fundamental parameters long established for a wide range of other metal atoms.

1. Introduction

There is both practical and fundamental interest in the characterization of the reaction kinetics of lead atoms. On fundamental grounds, particular attention is focused on the potential surfaces involved in collision and the

change of correlation between reactants and products based on the weak spin–orbit coupling approximation for the lighter Group IV atoms [1, 2], and (J, Ω) coupling for heavy atoms such as lead [3]. There is also, of course, extensive applied interest in the reactions of lead species at elevated temperatures in view of the "antiknock" effect arising from additives such as $Pb(C_2H_5)_4$ in internal combustion engine fuel [4, 5]. Whilst detailed calculations have been carried out of both final products and transient lead-containing species arising in engine combustion of fuel containing $Pb(C_2H_5)_4$, including the effects of chlorinated and brominated lead scavengers, these have been thermodynamic in nature and have not involved fundamental kinetic data [6]. For the high temperature medium of flames, modelling has been principally concerned with equilibria involving lead atoms, hydrogen atoms and OH and has included measurements on atomic chemiluminescence [7] and fluorescence quenching for $Pb(6p7s(^3P_1^\circ))$ [8]. Atomic absorption spectroscopic measurements on lead atoms in such a modelled medium have also been used to determine the bond dissociation energy of PbO [9]. Absolute rate data for the reactions of lead atoms have not, however, resulted from such measurements.

The various techniques designed to isolate fundamental processes have only been applied to atomic lead to a very limited extent. Absolute rate data for lead atoms have not, as yet, resulted from the highly sophisticated but experimentally demanding method of the fast flow reactor, so successful in the investigation of a wide range of other metal atom reactions [10, 11]. Studies of chemiluminescence from $PbO(a \rightarrow X, b \rightarrow X)$, resulting from a molecular beam study of $Pb + O_3$ [12] and in a flow system at higher pressures [13], have primarily been concerned with the spectroscopic aspects of the investigation. More recently, Wicke *et al.* [14] have reported relative chemiluminescence reaction cross sections to yield $PbO(B, v' = 0 \rightarrow X)$ from collision of N_2O with lead atoms with up to about 3 eV kinetic energy, derived from Q-switched ruby laser vapourization of thin metal films. It is only very recently that absolute rate constants for $Pb(6\,^3P_0)$ at elevated temperatures resulting from direct measurements have been reported, by the present authors, for removal by alkyl bromides [15] and N_2O [16]. Time-resolved atomic resonance absorption spectroscopy was employed, the $Pb(6\,^3P_0)$ being derived from pulsed irradiation of a halide vapour in a static reactor operating at elevated temperatures, with relatively high pressures of reactant gas, typically up to about 200 mbar (1 mbar $\equiv 100$ N m^{-2}). This is a development following the earlier work of Husain and Plane [17] on alkali atoms, and is now applied to the study of reactions of $Pb(6\,^3P_0)$ with CH_3Cl, C_2H_5Cl, n-C_3H_7Cl and SF_6, at elevated temperatures. Halogen atom abstraction reactions for many molecules of interest are rapid at the temperatures of flames and engines but are technically beyond measurement at such temperatures. At room temperatures, the abstraction rates are very slow, again beyond present experimental techniques. At reduced elevated temperatures, the rate constants are relatively low, principally on account of energy barriers (see later), but measurable with the present system. Thus the time-

resolved method capable of employing significant pressures of reactants at elevated temperatures is the most convenient compromise available for isolating the reactions in question. The Arrhenius parameters derived from the absolute second-order rate data for the above molecules are compared, where appropriate, with those for the bromine-containing analogues.

2. Experimental details

The experimental arrangement essentially follows that described in our previous investigations of ground state lead atoms at elevated temperatures [15, 16], with limited modifications for the individual reactant systems. Thus, $Pb(6\,^3P_0)$ was generated by the pulsed irradiation of $PbBr_2$ vapour in equilibrium with its solid in the temperature range 595 - 812 K [18 - 21]. The choice of this particular lead halide as the single photochemical precursor was governed by the temperature range available to this particular technique. At the high temperature end, $PbBr_2$ may be employed without significant thermal decomposition [18, 19] under the conditions chosen. Furthermore, $PbBr_2$ has a vapour density [18, 19] at the low end of the temperature range sufficient to yield $Pb(6\,^3P_0)$ at concentrations suitable for time-resolved spectroscopy in the "single-shot mode" following low energy flash photolysis ($E \approx 16$ J, 2 μF, 4 kV). This use of low energies has been shown to be necessary to avoid secondary processes resulting from the photolysis of the alkyl bromides employed previously [15]. The effect will be reduced even further here, with the absorption spectra of the alkyl chlorides shifted to lower wavelengths [22]. We have previously given a detailed account of the effect of absorption of actinic radiation by the alkyl bromides from the pulsed photolysis source [15] so further details are not repeated here for the similar effects, of considerably lower magnitude, for the chlorides. The time spent by the reactant gas in the high temperature reactor prior to photolysis is sufficiently long (several seconds) for thermal equilibration to be established by heat transfer to the walls but sufficiently short to avoid halogen exchange with the precursor. This is borne out by the consistency of the Arrhenius parameters, particularly the Arrhenius A factors (see later), which are of the magnitudes expected for atom−molecule collisions using the reactant densities of the halide gases described here. It is also sufficiently short to avoid thermal decomposition of the alkyl chlorides themselves at these temperatures [23]. The pure reactant gases at different pressures were admitted to the quartz reactor, with heated end windows to avoid condensation, by means of a magnetic plug arrangement described previously [15 - 17]. The use of pure reactant gases at relatively high concentration was necessary in order to ensure that chemical removal of $Pb(6\,^3P_0)$ by the alkyl chlorides and SF_6, characterized by relatively low rate constants at these temperatures (see later), dominated diffusional loss of $Pb(6\,^3P_0)$ to the walls of the reactor. The rate data are analysed in a form which takes quantitative account of diffusional loss.

Pb($6\,^3P_0$) was thus monitored by resonance absorption at $\lambda = 283.3$ nm (Pb($7s(^3P_1^\circ)$) $\leftarrow$ Pb($6p^2(^3P_0)$)), $gA = 1.8 \times 10^8$ s^{-1} [24]) on a time scale (about 10 - 50 ms) long compared with that for relaxation of any higher lying spin–orbit state of the $6p^2$ configuration (Pb($6\,^3P_1$), 0.969 eV; Pb($6\,^3P_2$), 1.320 eV [25]) [26] generated on photolysis. The resonance source comprised a high spectral output hollow cathode lamp (Westinghouse, U.S.A., 1000 V), optically isolated by means of a small monochromator of limited resolution (Grubb Parsons M2 monochromator), with photoelectric monitoring (EMI 9783B photomultiplier tube) under conditions in which the Beer–Lambert law may be applied. Thus the transmitted intensity I_{tr} describing an overall first-order decay for Pb($6\,^3P_0$) of coefficient k' may be expressed in the form

$$I_{tr} = I_0 \exp\{-A \exp(-k't)\} \tag{1}$$

(where I_0 is the unattenuated resonance signal) following the procedure of Clark and Husain [27, 28], yielding k', the object of experimental interest for a given decay. The photoelectric signals representing resonance absorption were amplified without distortion [29], captured, digitized and stored in a transient recorder (Data Laboratories DL 905), operating in the "A/B" mode in order to monitor the attenuated and unattenuated signals on different time scales (see Section 3), and transferred to paper-tape (Data Dynamics Punch 1183) for subsequent analysis on the University of Cambridge IBM 3081 computer following the previous procedure [15, 16]. Cylinder CH$_3$Cl (Matheson) was trapped at liquid nitrogen temperature (-196 °C), thoroughly degassed by a number of freeze–pump–thaw (FPT) cycles and fractionally distilled from a CO$_2$–acetone bath (-80 °C) to -196 °C. C$_2$H$_5$Cl (BDH) and n-C$_3$H$_7$Cl (AnalaR) were frozen at -196 °C, degassed by subjection to many FPT cycles and finally purified by fractional distillation, C$_2$H$_5$Cl from a CCl$_4$ slush (-22 °C) to -196 °C and n-C$_3$H$_7$Cl from an ice–water bath (0 °C) to -196 °C. SF$_6$ was prepared as described previously [30].

3. Results and discussion

Figure 1 gives examples of the digitized time variation of the transmitted light intensity at $\lambda = 283.3$ nm (Pb($7\,^3P_1^\circ$) $\rightarrow$ Pb($6\,^3P_0$)) representing the decay of resonance absorption by ground state lead atoms at various temperatures in the range 628 - 819 K following the low energy pulsed irradiation of PbBr$_2$ vapour in the presence of an approximately constant excess pressure of pure CH$_3$Cl. Pressure, as opposed to concentration, is chosen as the reactant variable in this investigation, for convenience in applying the diffusional correction in the analysis. Although the decay traces are long lived (Fig. 1) the removal rate increases significantly with temperature, as seen particularly from the comparison of Figs. 1(a) and 1(d). Of the "A" sweep of the transient recorder (AC), the portion BC is analysed by computer, corresponding to degrees of light absorption by Pb($6\,^3P_0$) of
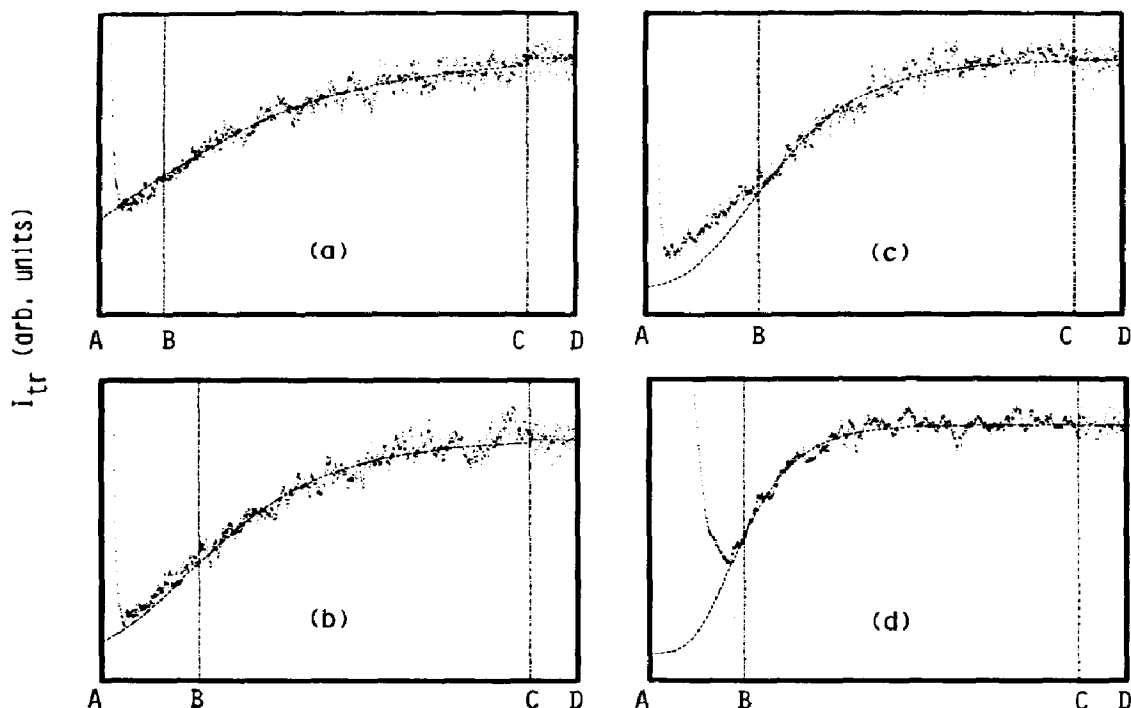
Fig. 1. Examples of the digitized time variation of the transmitted light intensity I_{tr} at $\lambda = $ 283.3 nm $(\text{Pb}(7s(^3P_1^\circ)) \to \text{Pb}(6p^2(^3P_0)))$ indicating the decay of resonance absorption by ground state lead atoms following the pulsed irradiation of PbBr_2 vapour in the presence of CH_3Cl ($E = 16$ J; abscissa labelling indicates the time base of the transient recorder (AC, A sweep; CD, B sweep; BC, portion of the A sweep analysed for the kinetic decay of $\text{Pb}(6\,^3P_0)$)): 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 $\text{Pb}(6\,^3P_0)$.

	$p_{\text{CH}_3\text{Cl}}$ (mbar)	AC (ms)	CD (s)	T (K)	k' (s^{-1})
(a)	140	46.2	1	628	76 ± 17
(b)	142	46.2	1	657	112 ± 24
(c)	140	46.2	1	709	145 ± 34
(c)	142	9.24	1	819	1230 ± 480

less than about 50%, where the Beer–Lambert law will be obeyed for the present optical resolution [15, 16]. CD indicates the "B" sweep of the transient recorder (1 s) from which the unattenuated signal (I_0) is derived. Further details of the analytical procedure for computerized fitting of the data of the type given in Fig. 1 to eqn. (1) yielding the overall first-order decay coefficient k' for the removal of $\text{Pb}(6\,^3P_0)$, in the presence of the alkyl chlorides and SF_6 in this case, may be found in our previous papers [15, 16].

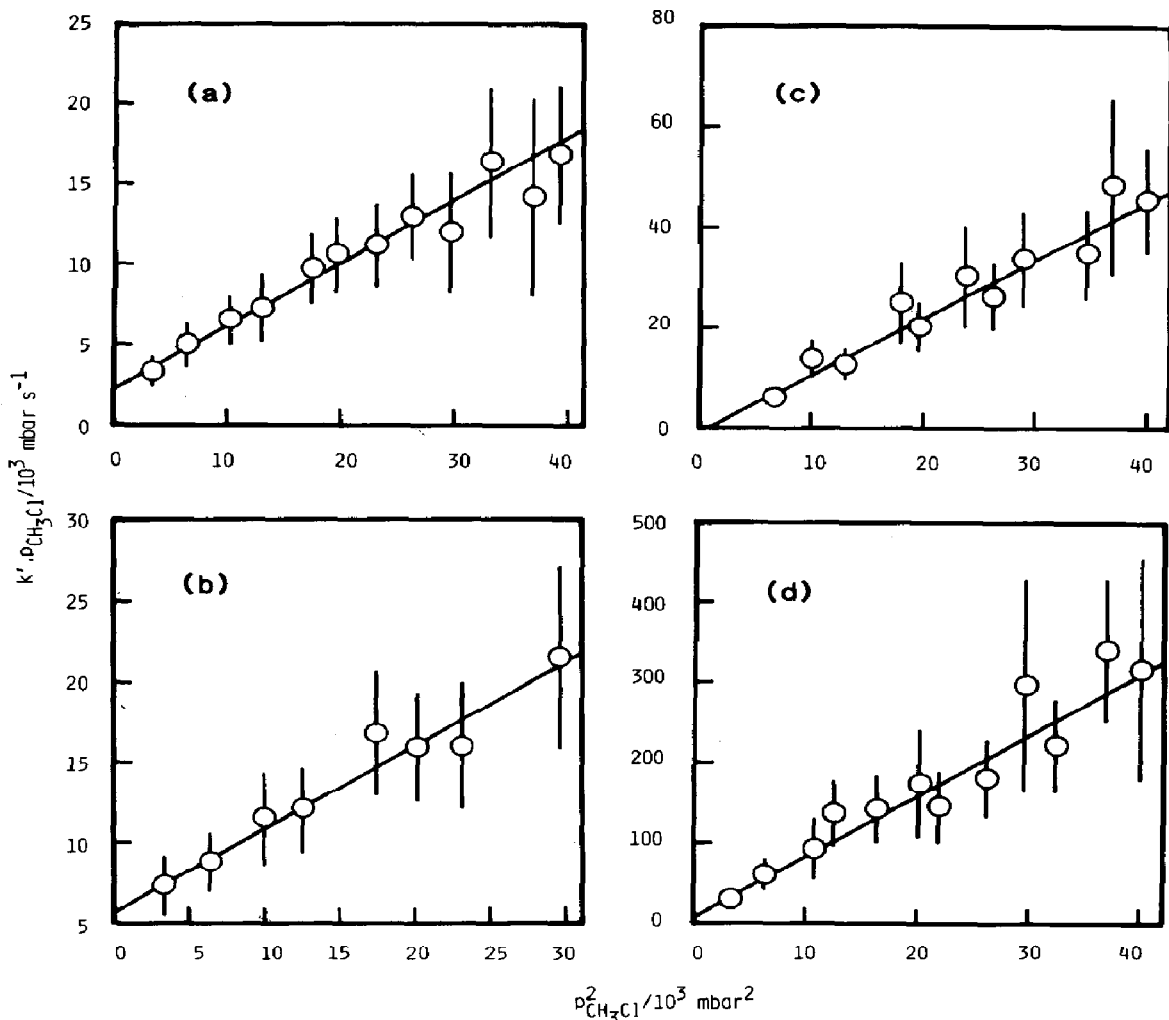k' for the removal of $\text{Pb}(6\,^3P_0)$ by the reactant RX both by chemical reaction

$$\text{Pb} + \text{RX} \xrightarrow{k_{\text{RX}}} \text{PbX} + \text{R} \tag{I}$$

Fig. 2. Variation of $k'p_{CH_3Cl}$ vs. $p_{CH_3Cl}^2$ of the pseudo-first-order rate coefficient k' for the decay of $Pb(6\,^3P_0)$ in the presence of CH_3Cl following the pulsed irradiation of $PbBr_2$ vapour at various temperatures indicating the removal of lead atoms by both chemical reaction and diffusion ($E = 16$ J): (a) $T = 628$ K; (b) $T = 657$ K; (c) $T = 709$ K; (d) $T = 819$ K.

and by diffusion may be expressed in the form [15, 16]

$$k' = \frac{\beta'}{p_{RX}} + k_{RX}p_{RX} \qquad (2)$$

where k_{RX} represents the absolute second-order rate constant for reaction (I) in the units of pressure and time at a given temperature. β' may be taken from the "long-time solution" of the diffusion equation for a long cylinder ($l \geqslant r$) [31, 32], namely

$$\frac{\beta'}{p_{RCl}} = \beta \approx \frac{5.81 D_{12}}{r^2} \qquad (3)$$

where D_{12} is the appropriate diffusion coefficient of Pb($6\,^3P_0$) in RX at a given temperature, and is inversely proportional to pressure. Since the object of the present investigation is the characterization of k_{RX}, eqn. (2) is recast in the form

$$k'p_{RX} = \beta' + k_{RX}p_{RX}^2 \qquad (4)$$

Figure 2 shows the variation of k' with p_{CH_3Cl} presented in the form of eqn. (4) for the examples of the four temperatures given in Fig. 1. The slopes of the plots in Figs. 2(a), 2(b), 2(c) and 2(d) yield the values of k_{CH_3Cl} at the temperatures 628 K, 657 K, 709 K and 819 K respectively. The intercepts, in principle, yield β' and hence D_{12}(Pb($6\,^3P_0$)–CH₃Cl) and, in general, the magnitudes are in approximate accord with those obtained hitherto for D_{12}(Pb($6\,^3P_0$)–He) as a function of temperature [15]. However, these intercepts are subject to large scatter as the objective of the present experimental system is to ensure the domination of chemical reaction over diffusional loss. The characterization of D_{12}(Pb–RX) would require measurement of the decay of Pb($6\,^3P_0$) at low pressures of RX and, in any event, the present system is not amenable to the determination of small differences between D_{12} for helium and RX. The experimental conditions are designed to characterize k_{RX} at different temperatures.

Decay traces for Pb($6\,^3P_0$), similar to those given in Fig. 1 for removal by CH₃Cl, were measured for C_2H_5Cl, n-C_3H_7Cl and SF_6 for various temperatures across the range available in this system. Figures 3, 4 and 5 give examples of the variation of k' with $p_{C_2H_5Cl}$, $p_{n\text{-}C_3H_7Cl}$ and p_{SF_6} respectively, each at two temperatures, in the form of eqn. (4) similar to the presentation of the data for CH₃Cl (Fig. 2). Table 1 lists the values of the absolute second-order rate constants k_{RX} for the removal of Pb($6\,^3P_0$) by CH₃Cl, C_2H_5Cl, n-C_3H_7Cl and SF_6 derived from the slopes of plots of the type given in Figs. 2 - 5 for the different temperatures employed in this investigation.

Figures 6 and 7 show the rate data given in Table 1 plotted in Arrhenius form ($k_{RX} = A\,\exp(-E_{act}/RT)$) and yielding the appropriate Arrhenius parameters. These are listed in Table 2 together with the analogous data for the alkyl bromides [15]. Before proceeding to a comparison of the data for the chlorides and bromides, we may conclude that the relatively large activation energies for chemical reaction of Pb + RX may be determined with sensible accuracy over what is necessarily a limited temperature range at elevated temperature and indeed constitute the first measurements of such fundamental rate data. The Arrhenius A factors, in accord with magnitudes expected for atom–molecule collisions and reflecting no significant effects of halogen exchange between the photochemical precursor and the reactants (see Section 2), are accurate to a factor of about 2 - 3. This inevitably arises from the extrapolation of k_{RX} to $1/T = 0$, derived from measurements at elevated temperatures over a limited temperature range, and applies to high temperature measurements in general.

Detailed consideration of the thermochemical data on which the thermochemistry of the halogen abstraction reactions of Pb($6\,^3P_0$) is based

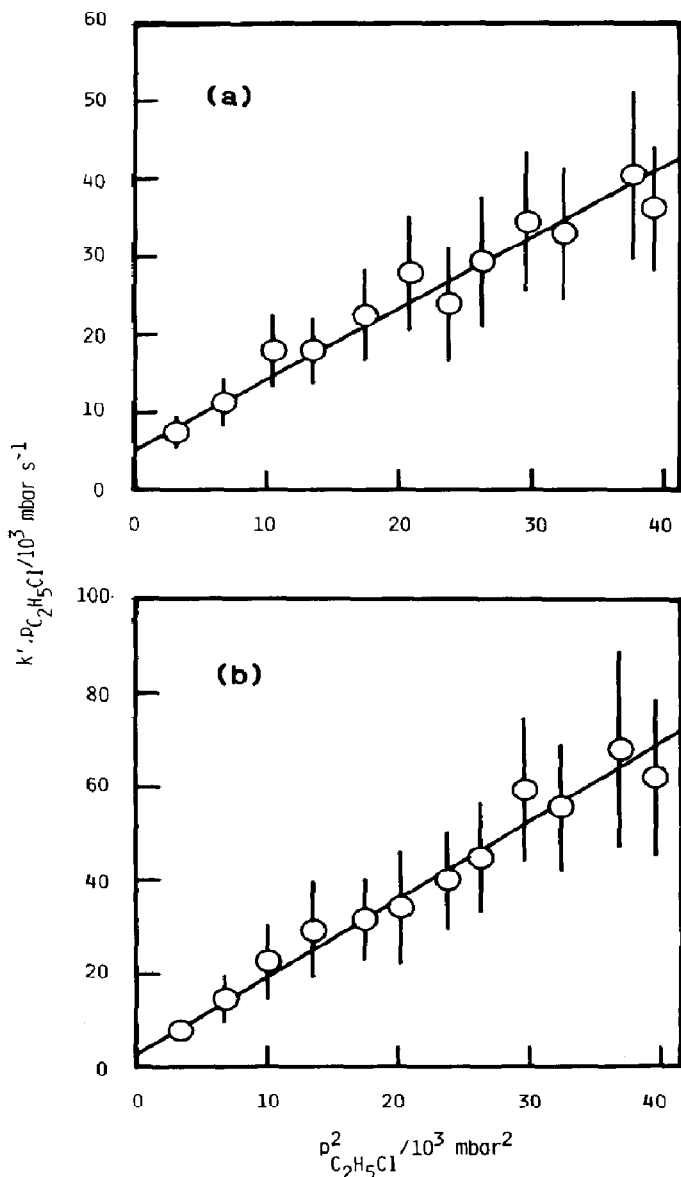Fig. 3. Variation of $k'p_{C_2H_5Cl}$ vs. $p^2_{C_2H_5Cl}$ of the pseudo-first-order rate coefficient k' for the decay of $Pb(6\,^3P_0)$ in the presence of C_2H_5Cl following the pulsed irradiation of $PbBr_2$ vapour at (a) $T = 652$ K and (b) $T = 704$ K indicating the removal of lead atoms by both chemical reaction and diffusion ($E = 16$ J).

is restricted, for the most part, to those bond dissociation energies where the results of different measurements are significant in the context of the measured activation energies. Bond dissociation energies for CH_3—Cl vary typically in the range 349 - 363 kJ mol^{-1} [33 - 35]. We employ the value of $D(CH_3$—Cl$) = 363$ kJ mol^{-1} on the basis of a weighted average of a large body of appearance potentials for CH_3^+ obtained from a wide range of mea-
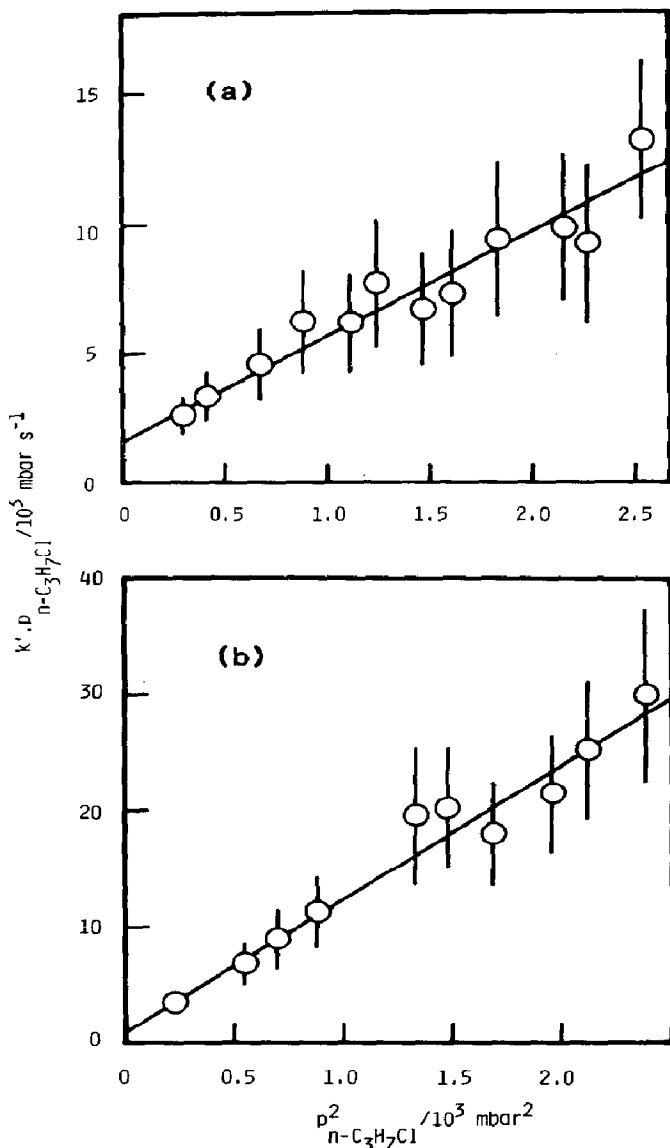
Fig. 4. Variation of $k'p_{n\text{-}C_3H_7Cl}$ vs. $p^2_{n\text{-}C_3H_7Cl}$ of the pseudo-first-order rate coefficient k' for the decay of $Pb(6\,^3P_0)$ in the presence of $n\text{-}C_3H_7Cl$ following the pulsed irradiation of $PbBr_2$ vapour at (a) $T = 649$ K and (b) $T = 711$ K indicating the removal of lead atoms by both chemical reaction and diffusion ($E = 16$ J).

surements [33]. Similar considerations for $C_2H_5^+$ yield $D(C_2H_5—Cl) = 339$ kJ mol^{-1} [33]. There is general agreement for this quantity from various measurements ($D(C_2H_5—Cl) = 339 - 341$ kJ mol^{-1} [33 - 35]). Appearance potential measurements yield a value for $D(n\text{-}C_3H_7—Cl)$ of 241 kJ mol^{-1} [33] which must clearly be regarded with caution and, accordingly, we employ $D(n\text{-}C_3H_7—Cl) = 341$ kJ mol^{-1} on the basis of thermochemical data [35]. The most critical choice for a bond dissociation energy in the present con-
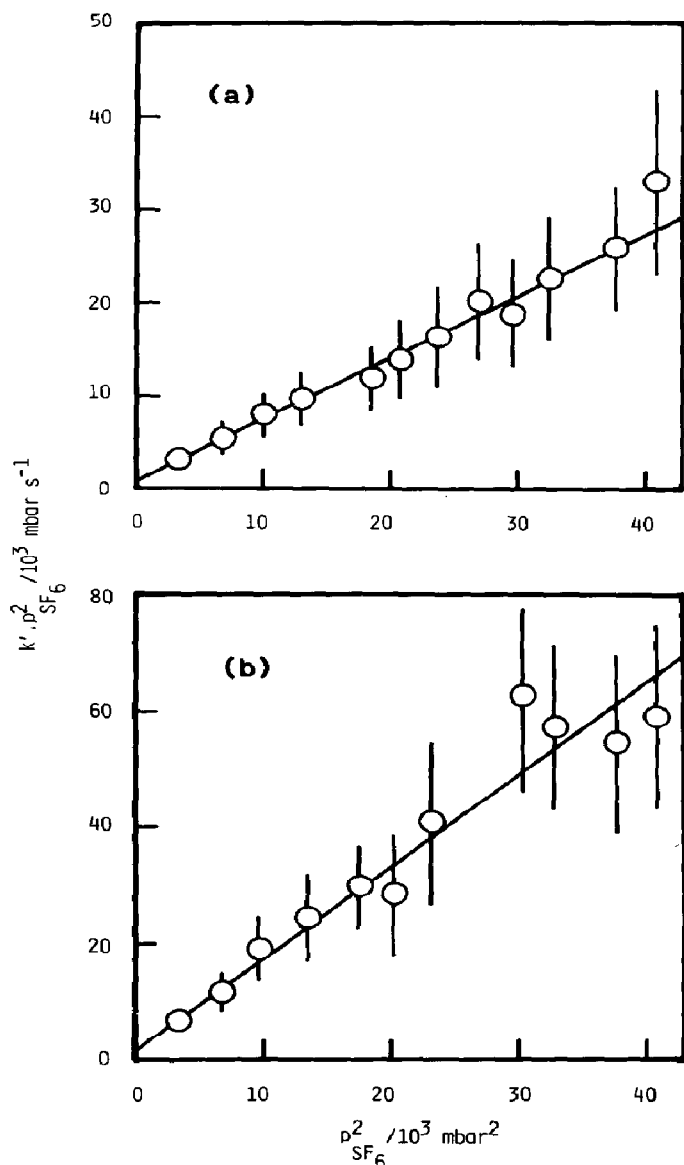
Fig. 5. Variation of $k'p_{SF_6}$ vs. $p^2_{SF_6}$ of the pseudo-first-order rate coefficient k' for the decay of $Pb(6\,^3P_0)$ in the presence of SF_6 following the pulsed irradiation of $PbBr_2$ vapour at (a) $T = 673$ K and (b) $T = 742$ K indicating the removal of lead atoms by both chemical reaction and diffusion ($E = 16$ J).

text concerns SF_6. Kiang *et al.* [36] have established the range of values for this property yielding $D(SF_5—F) = 376 \pm 14$ kJ mol^{-1}, on the basis of molecular chemiluminescence measurements resulting from the collisions of $Ca(4\,^3P_J)$ and $Sr(5\,^3P_J)$ with SF_6. This supersedes lower values ($D(SF_5—F) = 324$ kJ mol^{-1} [37]) based on thermochemical data. There is essentially agreement for $D^0_0(PbCl(X\,^2\Pi_{3/2})) = 299$ kJ mol^{-1} from the com-

TABLE 1

Absolute second-order rate constants k_{RX} for the reaction of Pb($6\,^3P_0$) with CH_3Cl, C_2H_5Cl, n-C_3H_7Cl and SF_6 at various temperatures determined by time-resolved atomic resonance absorption spectroscopy following pulsed irradiation of $PbBr_2$ vapour (errors, 1σ)

T (K)	k_{RX} ($\times 10^{-17}$ cm^3 molecule^{-1} s^{-1})
CH$_3$Cl	
594	1.52 ± 0.21
628	3.40 ± 0.15
657	4.72 ± 0.38
664	5.56 ± 0.37
709	11.2 ± 0.83
779	51.9 ± 2.5
819	85.8 ± 6.0
C$_2$H$_5$Cl	
614	2.52 ± 0.36
627	2.93 ± 0.15
647	6.22 ± 0.36
652	8.18 ± 0.47
666	6.86 ± 0.42
673	15.7 ± 1.3
704	16.2 ± 0.63
735	31.1 ± 1.7
n-C$_3$H$_7$Cl	
595	10.6 ± 1.5
624	19.9 ± 1.0
649	36.4 ± 2.4
678	61.9 ± 1.1
711	112 ± 5.1
711	133 ± 11
744	149 ± 8.9
794	290 ± 22
SF$_6$	
619	1.66 ± 0.23
659	1.74 ± 0.23
673	6.14 ± 0.20
702	6.88 ± 0.21
742	16.3 ± 0.90
765	28.7 ± 1.6
786	55.4 ± 4.4
812	85.5 ± 2.1

pilations of Huber and Herzberg [38] and Gaydon [39]. For PbF, we employ $D_0^\circ(PF(X\,^2\Pi_{3/2})) = 3.64$ eV (351 kJ mol^{-1}) following Huber and Herzberg [38] on the basis of the mass spectrometric measurements of Zmbov *et al.* [40]. This is compared with the value based on Gaydon's compilation,
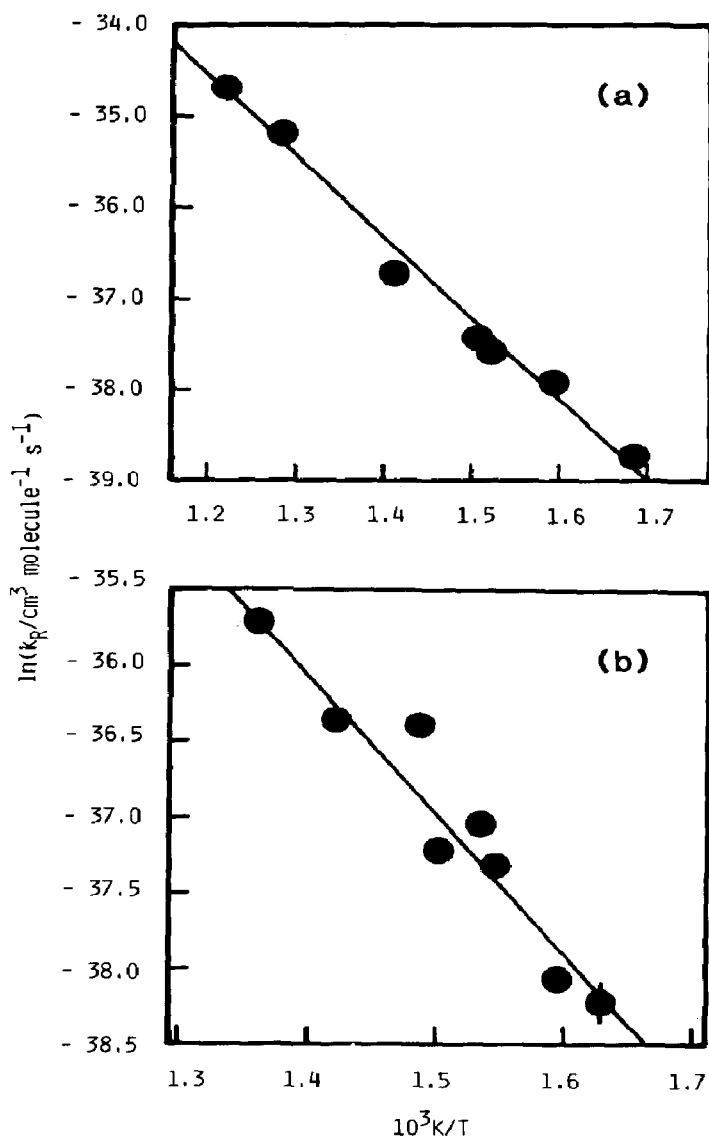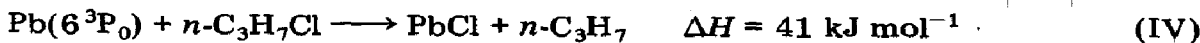
Fig. 6. Arrhenius plots (ln k_R vs. $1/T$) for the reaction of Pb(6^{3}P$_0$) with (a) CH$_3$Cl and (b) C$_2$H$_5$Cl.

$D_0^\circ(\text{PF}(X\,^2\Pi_{3/2})) = 3 \pm 0.5$ eV $(290 \pm 50$ kJ mol$^{-1})$ [39], the wide range for the two limits resulting from variations in the interpretation of the appropriate linear Birge–Sponer extrapolations and the predissociation in the spectra. The bond energies thus yield the following thermochemistries:

$$\text{Pb}(6\,^3\text{P}_0) + \text{CH}_3\text{Cl} \longrightarrow \text{PbCl} + \text{CH}_3 \qquad \Delta H = 64 \text{ kJ mol}^{-1} \qquad \text{(II)}$$

$$\text{Pb}(6\,^3\text{P}_0) + \text{C}_2\text{H}_5\text{Cl} \longrightarrow \text{PbCl} + \text{C}_2\text{H}_5 \qquad \Delta H = 40 \text{ kJ mol}^{-1} \qquad \text{(III)}$$

$$\text{Pb}(6\,^3\text{P}_0) + n\text{-C}_3\text{H}_7\text{Cl} \longrightarrow \text{PbCl} + n\text{-C}_3\text{H}_7 \qquad \Delta H = 41 \text{ kJ mol}^{-1} \qquad \text{(IV)}$$
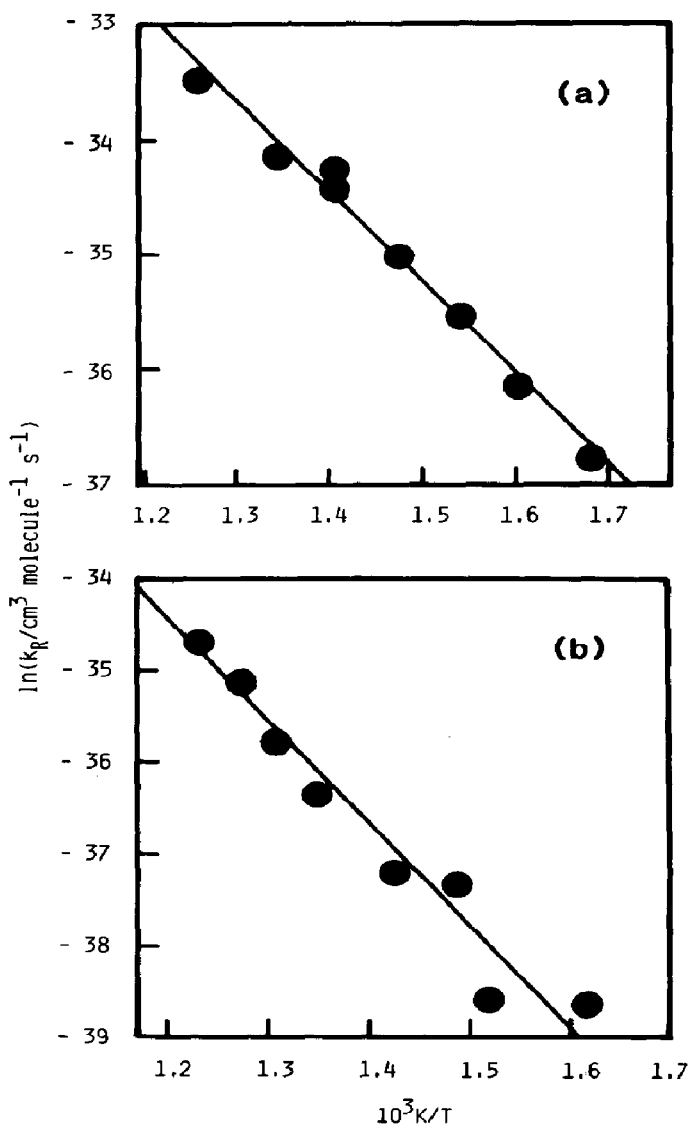
Fig. 7. Arrhenius plots (ln k_R vs. $1/T$) for the reaction of $Pb(6\,^3P_0)$ with (a) $n\text{-}C_3H_7Cl$ and (b) SF_6.

$$Pb(6\,^3P_0) + SF_6 \longrightarrow PbF + SF_5 \qquad\qquad \Delta H = 25 \text{ kJ mol}^{-1} \qquad\qquad (V)$$

The activation energies are significantly higher than the reaction endo-thermicities (Table 2) to extents comparable with those found previously for bromine atom abstraction with alkyl bromides. Thus, for example, the heat of reaction for the process analogous to reaction (II) between $Pb(6\,^3P_0)$ + CH_3Br is given by $\Delta H = 50 \pm 42 \text{ kJ mol}^{-1}$ [15]. The differences between the values of E_{act} for lead atoms plus CH_3Cl, C_2H_5Cl and $n\text{-}C_3H_7Cl$, coupled with the errors from the measurements across the restricted temperature range, are not sufficiently significant for further detailed consideration other than

TABLE 2

Arrhenius parameters ($k_{RX} = A \exp(-E_{act}/RT)$) for some halogen abstraction reactions by ground state lead atoms, $Pb(6\,^3P_0)$, determined at elevated temperatures by time-resolved atomic resonance absorption spectroscopy following the pulsed irradiation of $PbBr_2$ vapour in the presence of the respective reactant, RX

RX	A ($\times 10^{-11}$ cm^3 molecule^{-1} s^{-1})	E_{act} (kJ mol^{-1})	Temperature range (K)
CH_3Cl	4.5 (2.0)	74.2 ± 3.8	594 - 819[a]
C_2H_5Cl	8.0 (4.5)	76.2 ± 8.4	614 - 735[a]
n-C_3H_7Cl	7.2 (1.9)	65.8 ± 3.5	595 - 794[a]
SF_6	74 (3.3)	93.0 ± 7.3	619 - 812[a]
CH_3Br	30 (2.3)	63.6 ± 4.8	640 - 760[b]
C_2H_5Br	56 (2.9)	68.3 ± 6.2	641 - 708[b]
n-C_3H_7Br	310 (1.8)	74.5 ± 4.3	628 - 709[b]

Errors: 1σ error in E_{act}; in parentheses, factoral error in A factor.
[a] This work.
[b] From ref. 15.

to note that the values are comparable and similar to those for bromine atom abstraction. The A factors for Pb + RCl are smaller than those for their RBr analogues and may reflect marginal effects due to differences in polarizibilities on collision via the cross sections. Again, we must note that the A factors determined from such measurements (Table 2) can only necessarily be given to within a factor of 2 or 3 and only very large effects for atomic reactions, reflecting the influence of, say, non-adiabatic transition probabilities [1 - 3], merit detailed discussion. We would stress, however, that the present paper coupled with our previous investigation [15] represents the first detailed measurement of halogen abstraction reactions undergone by lead atoms at elevated temperatures, leading to characterization of the Arrhenius parameters, fundamental properties that have long constituted basic kinetic parameters for atoms in general [1, 41] and are now obtained for $Pb(6\,^3P_0)$ in particular.

Acknowledgments

References

1 R. J. Donovan and D. Husain, *Chem. Rev.*, 70 (1970) 489.

2 K. E. Shuler, *J. Chem. Phys.*, *21* (1953) 624.
3 D. Husain, *Ber. Bunsenges. Phys. Chem.*, *81* (1977) 168.
4 W. L. Richardson, P. R. Ryason, G. J. Kautsky and M. R. Barusel, *Proc. 9th Int. Symp. on Combustion*, Academic Press, New York, 1963, p. 1023.
5 H. van Gulick, *J. Automot. Eng.*, *6* (1975) 11.
6 Ting-Man Li and R. F. Simmons, *Combust. Flame, 56* (1984) 113.
7 P. J. Padley and T. M. Sugden, *Proc. 7th Int. Symp. on Combustion*, Butterworth, London, 1959, p. 235.
8 D. R. Jenkins, *Proc. R. Soc. (London), Ser. A, 313* (1969) 551.
9 N. J. Friswell and D. R. Jenkins, *Comb. Flame, 19* (1972) 197.
10 A. Fontijn and W. Felder, in D. W. Setser (ed.), *Reactive Intermediates in the Gas Phase*, Academic Press, New York, 1979, p. 59.
11 A. Fontijn and M. A. A. Clyne, *Reactions of Small Transient Species: Kinetics and Energetics*, Academic Press, London, 1983, p. 18.
12 R. C. Oldenborg, C. R. Dickson and R. N. Zare, *J. Mol. Spectrosc.*, *58* (1975) 283.
13 M. K. Kurylo, W. Braun, S. Abrahamovitz and M. Krauss, *J. Res. Natl. Bur. Stand., Sect. A, 80* (1976) 167.
14 B. G. Wicke, S. P. Tange and J. F. Friichenicht, *Chem. Phys. Lett.*, *53* (1978) 304.
15 D. Husain and I. P. Sealy, *J. Photochem.*, *30* (1985) 387.
16 D. Husain and I. P. Sealy, *J. Photochem.*, to be published.
17 D. Husain and J. M. C. Plane, *J. Chem. Soc., Faraday Trans. II, 78* (1982) 163.
18 M. N. Spiridonova, Yu. A. Aleksandrov and B. V. Emel'yanov, *Tr. Khim. Tekhnol., 1* (1971) 212.
19 R. C. Weast (ed.), *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 1983, 64th edn., p. D-196.
20 I. G. Murgulescu and E. Ivana, *Rev. Roum. Chim.*, *18* (1973) 1667.
21 I. G. Murgulescu and E. Ivana, *Rev. Roum. Chim.*, *21* (1975) 169.
22 J. G. Calvert and J. N. Pitts, *Photochemistry*, Wiley, New York, 1966, pp. 265, 523.
23 P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions*, Wiley-Interscience, New York, 1972, p. 222.
24 C. H. Corliss and W. R. Bozmann, Experimental transition probabilities for spectral lines of seventy elements, *Natl. Bur. Stand. (U. S.), Monogr., 53* (1962) 289.
25 C. E. Moore (ed.), Atomic Energy Levels, *Natl. Bur. Stand. Circ. 467*, Vols. 1 - 3, U.S. Govt. Printing Office, Washington, DC, 1958.
26 D. Husain and J. G. F. Littler, *Int. J. Chem. Kinet.*, *6* (1974) 61.
27 R. H. Clark and D. Husain, *J. Photochem.*, *24* (1984) 103.
28 R. H. Clark and D. Husain, *J. Chem. Soc., Faraday Trans. II, 80* (1984) 97.
29 W. H. Wing and T. M. Saunders, Jr., *Rev. Sci. Instrum.*, *38* (1962) 1341.
30 D. Husain and J. G. F. Littler, *J. Chem. Soc., Faraday Trans. II, 68* (1972) 2110.
31 A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms*, Cambridge University Press, London, 1961, p. 92.
32 M. W. Zemansky, *Phys. Rev.*, *34* (1929) 213.
33 J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron and K. Draxl, Ionisation Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions, *Natl. Bur. Stand., Rep. NSRDS-NBS-26*, U.S. Government Printing Office, Washington, DC, 1969, pp. 29, 31, 38, 40.
34 J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, New York, 1970, p. 400.
35 S. W. Benson, *Thermochemical Kinetics*, Wiley, New York, 1969, p. 309.
36 T. Kiang, R. C. Estler and R. N. Zare, *J. Chem. Phys.*, *70* (1979) 525.
37 V. I. Vedeneyev, L. V. Gurvich, V. N. Kondratiev, V. A. Medvedev and Ye.-L. Frankevich, *Bond Energies, Ionisation Potentials and Electron Affinities*, Nauka, Moscow, 1974, p. 110.
38 K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure,* Vol. IV, *Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1979, p. 525.

39 A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules,* Chapman and Hall, London, 1968, p. 280.
40 K. Zmbov, J. W. Hastie and J. L. Margrave, *Trans. Faraday Soc., 64* (1968) 861.
41 J. A. Kerr and S. J. Moss (eds.), *Handbook of Bimolecular and Termolecular Reactions,* Vol. 1, CRC Press, Boca Raton, FL, 1981, p. 151.