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KINETIC STUDY OF ELECTRONICALLY EXCITED ARSENIC ATOMS, As(4^2D$_J$, 4^2P$_J$), BY TIME-RESOLVED ATTENUATION OF ATOMIC RESONANCE RADIATION

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Summary

A method is described for the kinetic study of electronically excited arsenic atoms, As(4^2D$_J$) and As(4^2P$_J$), generated by pulsed irradiation and monitored photoelectrically in absorption by attenuation of atomic resonance radiation. Experimental conditions have been found in which removal of the ^{2}D and ^{2}P states may be treated as single kinetic decay processes. Detailed measurements on the individual J levels of the ^{2}D (J = 3/2 and 5/2) and ^{2}P (J = 1/2 and 3/2) states indicate that these are maintained in a Boltzmann equilibrium throughout the decay times. Collisional quenching data are reported for the parent photochemical sources, AsCl$_3$ and AsMe$_3$, and for the collisional partners H$_2$ and CO. The results are compared with previous data derived from plate photometric measurements, and with data on the analogous states, N(2^2D$_J$, 2^2P$_J$) and P(3^2D$_J$, 3^2P$_J$). The results are discussed within the framework of correlations based on considerations of spin and orbital symmetry.

Introduction

There is a developing interest in the direct study of the collisional behaviour of atoms in low lying electronic states [1, 2]. A vehicle, which has guided much of the experimental work in this area and which has provided a unifying theme for considering atomic reactions in general, is that of correlating specific states of reactants and products through the "least symmetrical complex" [3] on collision [4]. An important aspect of such a development is to elucidate the kinetic behaviour of different atoms of a given gross electronic structure within a given group of the periodic table. Thereby, one may investigate the effect of spin orbit coupling on correlations which are normally based on the weak spin orbit coupling approximation [4]. In the present context, we are concerned with the low lying states arising from the np^3 configurations in Group V, in particular, the electronically excited states, n^2D$_J$ and n^2P$_J$ above the n^4S$_{3/2}$ ground state.

Kinetic data for electronically excited nitrogen atoms, $N(2^2D_J)$ and $N(2^2P_J)$, derived from atomic absorption spectroscopic studies, have been reported by Lin and Kaufman [5] who employed a flow discharge system, and by Husain *et al.* [6] who used time-resolved measurements following pulsed irradiation. More recently, Acuna *et al.* [7 - 9] have obtained an extensive body of collisional rate data for $P(3^2D_J)$ and $P(3^2P_J)$, obtained from direct spectroscopic measurements on these atomic states in the time-resolved mode. In this paper, we present the results of kinetic investigations on electronically excited arsenic atoms, $As(4^2D_J)$ and $As(4^2P_J)$, respectively 1.333 and 2.283 eV above the $4^4S_{3/2}$ ground state [10]. Basco and Yee [11] have detected $As(4^2D_J)$ photographically in absorption, and Callear and Oldman [12] have reported rate data for $As(4^2D_{3/2})$, derived from plate photometry of atomic resonance lines following flash photolysis. We describe here a highly sensitive method for directly investigating the kinetic behaviour of both $As(4^2D_J)$ and $As(4^2P_J)$, generated by pulsed irradiation and monitored photoelectrically in absorption by time-resolved attenuation of atomic resonance radiation. Measurements on the individual spin orbit levels, $4^2D_{3/2,5/2}$ and $4^2P_{1/2,3/2}$, are also described. The resulting collisional rate data are compared with those for the analogous states of nitrogen and phosphorus and discussed within the context of spin and orbital symmetry [4].

Experimental

The general experimental arrangement for studying transient atoms, generated by pulsed irradiation and monitored photoelectrically in absorption by time-resolved attenuation of atomic resonance radiation, has been given hitherto for a number of atomic states, of which the system described for investigating $P(3^2D_J)$ and $P(3^2P_J)$ is typical [7]. Recent examples of studying metal atoms by this general method include the series of investigations of all the low lying states of atomic lead within the $6p^2$ configuration, namely, $Pb(6^3P_{0,1,2}, 6^1D_2$ and $6^1S_0)$, carried out by Husain and Littler [13 - 16]. $As(4^2D_J)$ and $As(4^2P_J)$ were generated by the flash photolysis of low pressures of suitable arsenic compounds, depending on the atomic state to be studied, in the presence of excess helium buffer gas ($\sim 10,000:1$) to ensure no significant rise in temperature on photolysis. The atomic states are highly optically metastable, as seen from the sum of the Einstein coefficients for spontaneous emission (ΣA) for the individual spin orbit levels to all lower accessible states [17]:

Atomic state	$E(\text{cm}^{-1})$ [10]	$\Sigma A(\text{s}^{-1})$ [17]
$4^2P_{3/2}$	18,648	2.71
$4^2P_{1/2}$	18,186	1.17
$4^2D_{5/2}$	10,915	3.84×10^{-3}
$4^2D_{3/2}$	10,592	7.49×10^{-2}
$4^4S_{3/2}$	0	—

and hence may be monitored in absorption *via* allowed electronic transitions to higher states.

A coaxial lamp and vessel assembly, similar to that described by Sorokin *et al.* [18] was employed. The inner cylinder comprised the reaction vessel, and the annular space, of thickness ~ 2 mm to facilitate an intense plasma discharge between machined brass electrodes, comprised the photoflash lamp which contained krypton gas [$p_{Kr} = 1.3$ kN/m^2 (1 Torr $= 133$ N/m^2)]. The lamp was fired by means of high voltage switching using an ignitron circuit (BK66, B.T.H., U.K.) ($E = 980$ J, $V = 14$ kV, $C = 10$ μF). Following photolysis, resonance lines connecting with As(4^2D_J) and As(4^2P_J), derived from a sealed microwave-powered arsenic atomic lamp (E.M.I. Cavity C111, incident power $= 50$ W) were isolated by means of a Seya–Namioka grating monochromator [19, 20] (radius of curvature of grating $= 500$ mm, blaze wavelength $= 110.0$ nm, 1180 lines/mm, MgF$_2$ coated). (We are deeply indebted to Mr. D. G. Oliver and Mr. R. Asby of the Engineering workshops of the Department of Physical Chemistry, the University of Cambridge, for the design and construction of this instrument.)

The following atomic transitions from the microwave-powered lamp were attenuated subsequent to photolysis:

Transition	λ(nm)	$10^{-8}gA(s^{-1})$ [21]
$5^2P_{1/2} \rightarrow 4^2P^0_{1/2}$	286.04	33.0
$5^2P_{3/2} \rightarrow 4^2P^0_{3/2}$	278.02	60.0
$5^2P_{1/2} \rightarrow 4^2D^0_{3/2}$	234.98	26.0
$5^2P_{3/2} \rightarrow 4^2D^0_{5/2}$	228.81	15.0

The time-resolved attenuated signals representing absorption by As(4^2D_J) and As(4^2P_J) were detected by means of a photomultiplier tube (PM tube, E.M.I. 9783B, Spectrosil envelope, tube voltage $= 560$ V) mounted on the exit slit of the monochromator. Whilst the half-life of the photoflash discharge was of duration ~ 20 μs, with the slit widths employed during kinetic experiments (250 - 300 μm), the effect of the scattered light on the photomultiplier was to prevent kinetic measurements from being made during the first 100 μs following the photoflash. Fortunately, the kinetic decays of As(4^2D_J) and As(4^2P_J) could be readily separated by the use of the appropriate parent molecules and the region of photolysis. As(4^2P_J) was generated by the irradiation of AsCl$_3$ at low pressures, using a Spectrosil tube as the inner cylinder reaction vessel in the coaxial arrangement, which permitted photolysis to be effected to a lower wavelength limit of $\sim \lambda = 160$ nm; As(4^2D_J) could be generated from the photolysis of AsMe$_3$ with a quartz reaction vessel ($\lambda > \sim 200$ nm), with an insignificant photolysis yield of As(4^2P_J). The pulses from the photomultiplier tube were stored in a transient recorder (Datalab DL 905). Hitherto, "single-shot" experiments of this type

on transient atoms, such as with the various states of atomic lead [13 - 16], involved transfer of the contents of the transient recorder onto an XY recorder with subsequent measurements on the resulting graphical display. A novel variation for this type of system was employed. The contents of the 1024 word memory of the recorder were punched onto paper tape in ASCII code (Datadynamics Punch 1133) for direct input into a computer (IBM 370) for analysis.

Materials

AsCl$_3$ liquid (British Drug Houses Ltd) was purified by fractional distillation under nitrogen and then degassed by many freeze–pump–thaw cycles at −196°. AsMe$_3$ liquid (Alfa Inorganic Chemicals Inc.) was also thoroughly degassed in a similar manner before use. Cylinder He (British Oxygen Company Ltd) was purified by passage through a standard B.O.C. purifier, capable of purifying both He and Ar. Kr (B.O.C. Grade X) (for the photoflash lamp), H$_2$ (B.O.C. Grade X) and CO (B.O.C. Grade X) were used directly.

Results and Discussion

The photoelectric pulses, representing the temporal variation of As(4^2D$_J$) and As(4^2P$_J$) following photolysis, and the kinetic plots derived from these pulses, were analyzed by means of the computer. Examples of the data at these stages in the calculation are given here in graphical form purely for the purpose of presentation. Figure 1 gives an example of the computerized output of the unsmoothed, digitized transmitted light intensity at λ = 234.98 nm [As(5^2P$_{1/2}$) → As(4^2D$^0_{3/2}$)], indicating the decay of resonance absorption by As(4^2D$_{3/2}$) following the photolysis of arsenic trimethyl (λ > 200 nm) in the presence of excess helium buffer gas. A delay of 100 μs was employed in order to remove the effect of scattered light from the photolysis pulse. As with previous experiments on resonance absorption by O(2^1D$_2$), which, in fact, involved signal averaging [22 - 26], the numerical data smoothing procedure of Savitsky and Golay [27] was followed in order to obtain maximum use of the data at low degrees of resonance light absorption. The modified Beer–Lambert law [28]:

$$I_{tr} = I_0 \exp\left[-\epsilon\,(cl)^\gamma\right] \tag{1}$$

(where the symbols have their usual significance) was then employed in order to translate the light intensity signals shown in Fig. 1 into relative concentrations of the ^{2}D state.

Figure 2 shows a computerized first-order plot {ln[ln(I_0/I_{tr})] *vs.* time} of the data presented in Fig. 1. The slope of this plot is given by $-\gamma k'$, where k' is the overall first-order decay coefficient for a given reaction mixture. Similar results to those given in Figs. 1 and 2 for As(4^2D$_{3/2}$) may be readily obtained for the other individual spin orbit levels investigated here, *viz.*
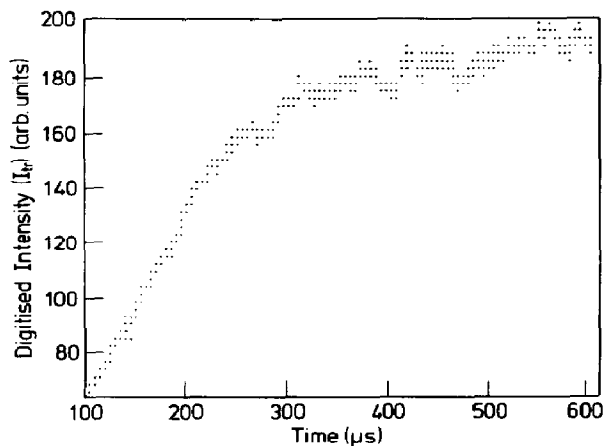
Fig. 1. Digitized time–variation of the transmitted light intensity at λ = 234.98 nm [As($5\,^2P_{1/2}$) → As($4\,^2D^0_{3/2}$)] indicating the decay of resonance absorption by As($4\,^2D_{3/2}$). p_{AsMe_3} = 0.33 N/m^2, $p_{total\ with\ He}$ = 6.67 kN/m^2; E = 980 J; recording delayed by 100 μs.
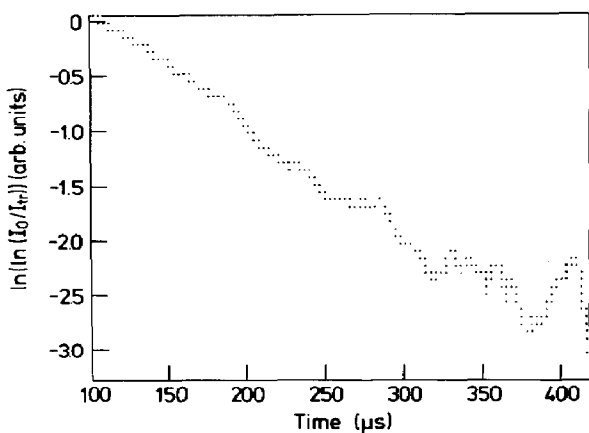

Fig. 2. Typical pseudo-first-order plot for the decay of As($4\,^2D_{3/2}$) obtained by monitoring the absorption of light at λ = 234.98 nm [As($5\,^2P_{1/2}$) ← As($4\,^2D^0_{3/2}$)]. p_{AsMe_3} = 0.33 N/m^2, $p_{total\ with\ He}$ = 6.67 kN/m^2; E = 980 J.

As($4\,^2D_{5/2}$) and As($4\,^2P_{1/2,3/2}$). As indicated in the experimental section, no significant concentration of As($4\,^2P_J$) was generated on photolyzing AsMe$_3$ in the quartz region (λ > 200 nm). As($4\,^2P_J$) was only generated in measurable concentrations when AsCl$_3$ was photolyzed through Spectrosil quartz (λ > 160 nm). We may therefore treat the measured removal rates of both states as separate kinetic decay processes. The variation of k' with reactant composition yields the collisional quenching data required, and therefore the γ values for the resonance transitions employed to monitor the four spin orbit levels are determined in order to obtain the absolute values of k' from plots of the type given in Fig. 2.

We employ the general method for the determination of the values of γ described previously for the transition at $\gamma = 113.2$ nm used to monitor $O(2^3P_J)$ [28]. In this case, we assume a proportionality between $[As(4^2D_J)]_{t=0}$ and $[As(4^2P_J)]_{t=0}$ and the low varying pressures of the arsenic compounds employed. This, combined with eqn. (1), yields the so-called Beer–Lambert plot of $\ln[\ln(I_0/I_{tr})]_{t=0}$ vs. $\ln(p_{As\ compound})$, the slope of which yields γ [28]. The difficulties encountered in employing this method have been described in a number of papers in which eqn. (1) has been used to obtain relative concentrations of various atomic states by the attenuation of resonance radiation, and much of this work has been reviewed recently [1, 2]. The series of kinetic investigations carried out on the $6^3P_{0,1,2}$, 6^1D_2 and 6^1S_0 states of lead [13 - 16] have emphasized the nature of these problems. Figures 3 and 4 show the Beer–Lambert plots for the resonance transitions employed here. Whilst there is some scatter in these plots, the observed errors indicate the satisfactory nature of the results, given in Table 1, for this type of measurement.

We now proceed to investigate the decay rates of the individual spin orbit levels. The collisional quenching rates are normally expressed in the form:

$$k' = K + k_Q[Q] \tag{2}$$

where k_Q is the second-order rate constant for collisional removal by a quenching gas, Q. K is taken to be a constant in a given series of kinetic runs and includes losses by diffusion, weak spontaneous emission, and removal by impurities, and products of photolysis. Figures 5 and 6 show the variation of
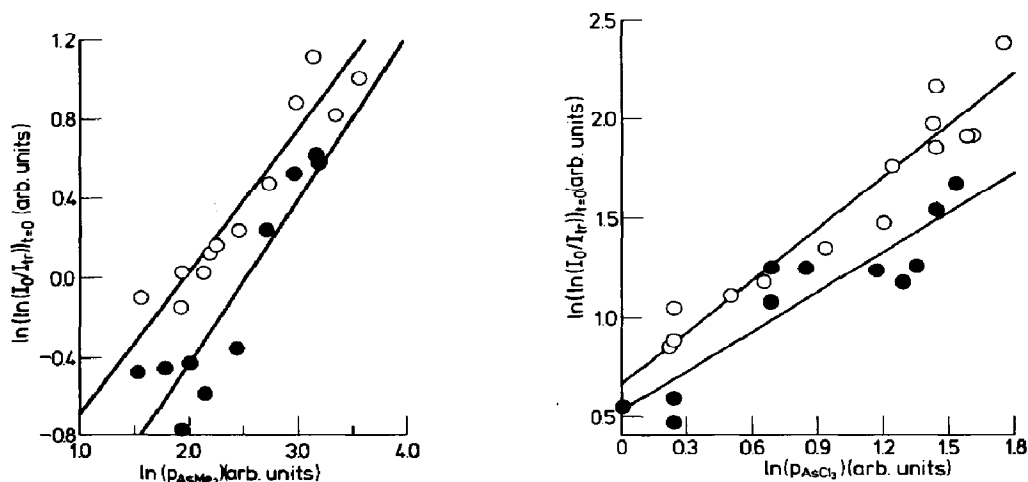

Fig. 3. Beer–Lambert plots for the absorption of resonance radiation by $As(4^2D_J)$. $\bigcirc$, $As(4^2D_{3/2})$ ($p_{total\ with\ He} = 6.67$ kN/m^2); $\lambda = 234.98$ nm; $\bullet$, $As(4^2D_{5/2})$ ($p_{total\ with\ He} = 3.33$ kN/m^2); $\lambda = 228.81$ nm.

Fig. 4. Beer–Lambert plots for the absorption of resonance radiation by $As(4^2P_J)$. $p_{total\ with\ He} = 3.33$ kN/m^2. $\bigcirc$, $As(4^2P_{1/2})$; $\lambda = 286.04$ nm; $\bullet$, $As(4^2P_{3/2})$; $\lambda = 278.02$ nm.

TABLE 1

γ-values for the resonance transitions employed to monitor As(4^2D_J) and As(4^2P_J)

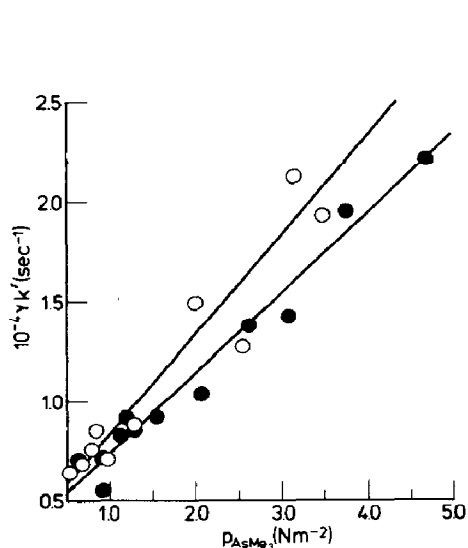| Transition			γ
$5^2P_{1/2}$	$\leftarrow 4^2D^0_{3/2}$	$(\lambda = 234.98 \text{ nm})$	0.70 ± 0.07 (Fig. 3)
$5^2P_{3/2}$	$\leftarrow 4^2D^0_{5/2}$	$(\lambda = 228.81 \text{ nm})$	0.83 ± 0.12 (Fig. 3)
$5^2P_{1/2}$	$\leftarrow 4^2P^0_{1/2}$	$(\lambda = 286.04 \text{ nm})$	0.86 ± 0.06 (Fig. 4)
$5^2P_{3/2}$	$\leftarrow 4^2P^0_{3/2}$	$(\lambda = 278.02 \text{ nm})$	0.67 ± 0.10 (Fig. 4)

Fig. 5. Plots of first-order rate coefficients ($\gamma k'$) for the decay of As($4^2D_{3/2}$) and As($4^2D_{5/2}$) against the pressure of $AsMe_3$.

●, As($4^2D_{3/2}$): $p_{\text{total with He}} = 6.67 \text{ kN/m}^2$; $E = 980 \text{ J}$.

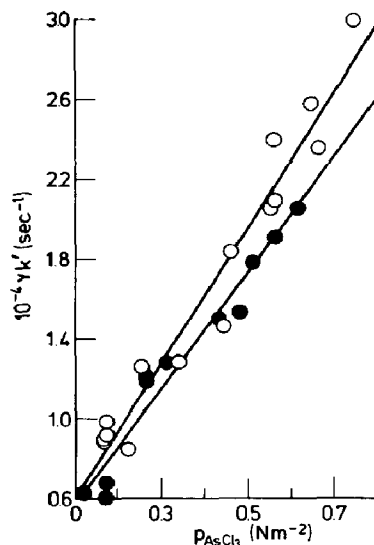○, As($4^2D_{5/2}$): $p_{\text{total with He}} = 3.33 \text{ kN/m}^2$; $E = 980 \text{ J}$.

Fig. 6. Plots of first-order rate coefficients ($\gamma k'$) for the decay of As($4^2P_{1/2}$) and As($4^2P_{3/2}$) against the pressure of $AsCl_3$. $p_{\text{total with He}} = 3.33 \text{ kN/m}^2$; $E = 980 \text{ J}$.

○, As($4^2P_{1/2}$); ●, As($4^2P_{3/2}$).

the first-order coefficients ($\gamma k'$) for the decays of the individual spin orbit levels as a function of the parent molecular concentrations. With the appropriate values of γ from Table 1, the slopes of these plots, following eqn. (2), yield the *effective* second-order rate constants for the removal of As($4^2D_{3/2,5/2}$) and As($4^2P_{1/2,3/2}$) (Table 2). The observed rates of removal for the two spin orbit levels in each state are clearly equal within experimental error. It may readily be shown that the measured values of k' for the separate spin orbit states would be equal if equilibrium is maintained between the J levels over

TABLE 2

Effective second-order rate constants (k_Q) for the collisional removal of $As(4\,^2D_{3/2,\,5/2})$ and $As(4\,^2P_{1/2,\,3/2})$.

J	k_Q (cm^3 molecule^{-1} s^{-1}, 300 K)
$As(4\,^2D_J)$:	
3/2	$2.4 \pm 0.1 \times 10^{-11}$ (AsMe$_3$)
5/2	$2.5 \pm 0.5 \times 10^{-11}$ (AsMe$_3$)
$As(4\,^2P_J)$:	
1/2	$1.6 \pm 0.2 \times 10^{-10}$ (AsCl$_3$)
3/2	$1.8 \pm 0.3 \times 10^{-10}$ (AsCl$_3$)

the kinetic decay, even if the individual rate constants out of the J levels into lower states were different. Callear and Oldman [12] found from spectro-photographic measurements at very short delay that the relaxation of $As(4\,^2D_{5/2} \rightarrow {}_{3/2})$ is very rapid and they estimated a relaxation cross-section (σ^2) with argon of 10^{-3} Å^2. General considerations of the magnitude of the energy to be transferred to translation [29] (^2D, J = 5/2 − 3/2 = 322 and ^2P, J = 3/2 − 1/2 = 461 cm^{-1}) [10] indicate that equilibrium between the J levels of the ^2D and ^2P states of arsenic should be maintained over these measurements. We assume that the collisional quenching rates for the two spin orbit levels out of a given state are equal on account of the close similarity in electronic structure. Hence the measured values of $k´$ may be used to obtain second-order quenching constants for the ^2D_J and ^2P_J states.

In view of the foregoing, we may thus restrict kinetic measurements on $As(4\,^2D_J)$ and $As(4\,^2P_J)$ to either of the two J levels and we have, in fact, chosen the lower one in each case. Whilst the transition at λ = 286.04 nm ($5\,^2P_{1/2} - 4\,^2P_{1/2}$) is characterized by a lower gA value than that for the J = 3/2 line at λ = 278.02 nm [21] (see experimental), in terms of light absorption, this is offset by the greater Boltzmann population in the lower J level. For the λ = 234.98 nm transition ($5\,^2P_{1/2} - 4\,^2D_{3/2}$), the gA value is greater than that for the line at λ = 228.81 nm (see experimental) and the lower J value again enjoys the larger Boltzmann population. On the other hand, the intensity of the latter line from the spectroscopic source is greater. We thus report data on the quenching of the ^2D_J and ^2P_J states by hydrogen and carbon monoxide. Figure 7 shows the results in the form of eqn. (2) for H_2, the slopes of these plots yielding k_{H_2} for $As(^2D_J)$ and $As(^2P_J)$. Similar results were obtained for CO. Table 3 lists the resulting second-order quenching constants for these gases which are compared with those derived from plate photometric measurements [12] and the previously published data for $P(3\,^2P_J, 3\,^2D_J)$ and $N(2\,^2D_J, 2\,^2P_J)$.
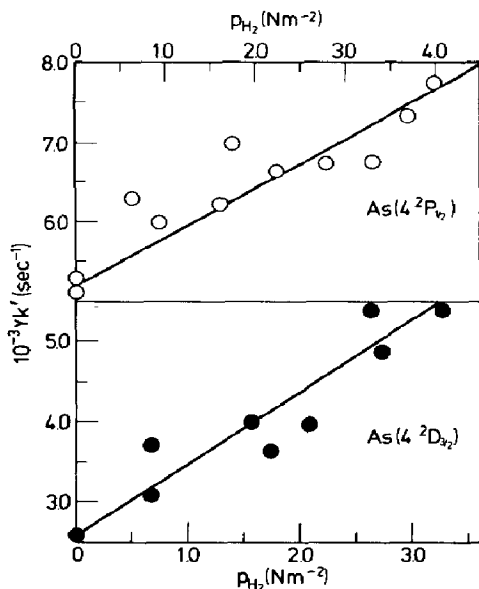
Fig. 7. Plots of the first-order rate coefficients ($\gamma k'$) for the decay of As($4^2D_{3/2}$) and As($4^2P_{1/2}$) against the pressure of hydrogen. As($4^2D_{3/2}$) : p_{AsMe_3} = 0.33 N/m^2, $p_{total\ with\ He}$ = 6.67 kN/m^2; E = 980 J. As($4^2P_{1/2}$): p_{AsCl_3} = 0.33 N/m^2, $p_{total\ with\ He}$ = 3.33 kN/m^2; E = 980 J.

TABLE 3

Rate constants for the collisional quenching of the ^2D_J and ^2P_J states of As, P and N (k, cm^3 molecule^{-1} s^{-1}, 300 K)

	H$_2$	CO
As(4^2D_J)	$5.1 \pm 0.8 \times 10^{-12}$ (this work)	$4.0 \pm 0.8 \times 10^{-11}$ (this work)
	$2.8 \pm 0.3 \times 10^{-11}$ (ref. 12)	$4.7 \pm 0.6 \times 10^{-11}$ (ref. 12)
As(4^2P_J)	$2.8 \pm 0.5 \times 10^{-12}$ (this work)	$5.1 \pm 0.8 \times 10^{-12}$ (this work)
P(3^2D_J)	$4.0 \pm 0.7 \times 10^{-12}$ (ref. 7)	$1.5 \pm 0.4 \times 10^{-11}$ (ref. 8)
P(3^2P_J)	$3.1 \pm 0.8 \times 10^{-13}$ (ref. 7)	$7 \pm 6 \times 10^{-16}$ (ref. 8)
N(2^2D_J)	$1.7 \pm 0.5 \times 10^{-12}$ (ref. 6)	6×10^{-12} (ref. 30)
	5×10^{-12} (ref. 5)	
N(2^2P_J)	$3.0 \pm 1.1 \times 10^{-15}$ (ref. 6)	—

The present result for the quenching of As(4^2D_J) by H$_2$ (Table 3) yields a rate which is a factor of five slower than that obtained by Callear and Oldmann [12] from plate photometric measurements. The high sensitivity (detection limit = $\sim 10^{-5}$ Torr) of the present method clearly indicates that the initial photochemical yield of As(4^2P_J) in the experiments

on the ^2D states was negligible (see earlier), and that no significant relaxation from the ^2P state into the ^2D state took place during this group of measurements. Furthermore, the concentrations of arsenic compounds and transient atoms are extremely small and quenching by photochemical fragments is negligible in this system. This would, indeed, increase the rate of removal. Beyond indicating this difference in rates, we offer no further explanation.

Donovan and Husain [4] had hitherto discussed the quenching of $As(4^2D_J)$ by H_2 in terms of spin and orbital symmetry. However, this was based on an upper limit for $D[As(X^3\Sigma^-)]$ reported by Dixon et al. [31], the most significant effect of which being, in the present context, that reaction of $As(4^2D_J) + H_2$ was considered to be exothermic. This must be revised in the light of later spectroscopic work on the $AsH(A^3\Pi - X^3\Sigma^-)$ system by Dixon and Lamberton [32]. To consider initially the cases of the quenching of the ^2D and ^2P states of phosphorus and nitrogen by hydrogen (Table 3), chemical reaction of both states of these two atoms would be exothermic, and the observed slower rates for the ^2P states of P and N were attributed to the absence of an orbital correlation to yield products exothermically [6, 7]. Dixon and Lamberton's analysis [32] of the $AsH(A^3\Pi - X^3\Sigma^-)$ system yielded an upper limit of $D_0^0[AsH(X^3\Sigma^-)]$ of 3.63 eV from the observation of predissociation in the spectrum but a limited extrapolation in the $A^3\Pi$ state gave $D(AsH) = 2.77 \pm 0.12_4$ eV, which is preferred by these authors [32]. On this latter basis, and on the basis of the estimated energies of $AsH(^1\Delta)$ (0.8 eV) and $AsH(^1\Sigma^+)$ (1.6 eV) [32], a correlation diagram for $As + H_2 = AsH + H$ may be readily constructed [4] and the nature of the correlations are found to be the same for the low lying states as found for $N + H_2 = NH + H$ [4] and $P + H_2 = PH + H$ [7]. By contrast with P and N, reaction of $As(4^2D_J)$ with H_2 is endothermic ($\Delta H = +0.378$ eV) but, of course, correlates with ground state products. As in the cases of $N(^2P) + H_2$ and $P(^2P) + H_2$, reaction would be exothermic but again, there is no thermochemically favourable correlation and a "non-adiabatic transition" [4] must occur on quenching. AsH was not observed spectroscopically in Callear and Oldman's experiments [12] and indeed, the relatively slow rate observed here for $As(^2D) + H_2$ is too fast to be accounted for in terms of an energy barrier of a magnitude equal to that of the above endothermicity for chemical reaction. We may only presume that the quenching rate of the ^2D state is facilitated by AsH_2, for which there will be an exothermic correlation with $AsH_2(X^2B_1)$, the system $AsH_2[A(^2A_1) \leftarrow X^2(B_1)]$ having been observed and analyzed by Dixon et al. [33].

There is good agreement between the present result for the quenching rate for $As(4^2D_J) + CO$ and that obtained by Callear and Oldman [12]. No previous rate measurement for $As(4^2P_J)$ with this molecule has been reported. Chemical reaction of both atomic states would be highly endothermic [34]. Donovan and Husain [4] have discussed the deactivation of the ^2D state. They have suggested that an intermediate AsCO, analogous to $NCO(\tilde{X}^2\Pi)$ [35], which is presumed to facilitate the rapid quenching of $N(2^2D_J)$ by CO [4 - 6],

may account for the relatively rapid deactivation in this case. Similar suggestions have been made for the relaxation of $P(3\,^2D_J)$ and $P(3\,^2P_J)$ by CO [8]. We would presume that the quenching of $As(4\,^2P_J)$ proceeds by means of the same mechanism.

Having established in detail the present method of monitoring very low concentrations of $As(4\,^2D_J)$ and $As(4\,^2P_J)$ over the complete decay times, and the use of this particular system for obtaining kinetic data for these states, future work will be directed towards measuring collisional quenching rate constants with various gases. Clearly, the effect of spin orbit coupling on the electronic correlations for the low lying atomic states within Group V will be investigated across a wide range of collision partners.

Acknowledgements

We thank Professor J. W. Linnet, F.R.S. for encouragement and laboratory facilities. We are indebted to the Science Research Council of Great Britain for a Studentship to one of us (M. J. B.), during the tenure of which this work was carried out, and for a grant for equipment.segment>

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