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Kinetic Studies of Ground-state Phosphorus Atoms

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The kinetics of reactions (at 293 K) involving ground-state phosphorus atoms $P(^4S_{3/2})$ have been studied using resonance-fluorescence detection in a discharge–flow system for the first time. P atoms were formed by means of a discharge in helium with a trace of phosphorus trihalide. The rate constants k (cm^3 $molecule^{-1}$ s^{-1}) (1σ) have been determined using pseudo-first-order kinetic analysis for the following reactions:

$$P+NO_2 \xrightarrow{k_1} PO+NO; \qquad k_1=(1.62\pm0.07)\times10^{-11}$$

$$P+O_2 \xrightarrow{k_2} PO+O; \qquad k_2=(9.9\pm0.2)\times10^{-14}$$

$$P+Cl_2 \xrightarrow{k_3} PCl+Cl; \qquad k_3=(7.0\pm0.4)\times10^{-13}$$

$$P+NO \xrightarrow{k_4} PN+O; \qquad k_4=(3.4\pm0.1)\times10^{-14}$$

$$P+Cl_3 \xrightarrow{k_5} \quad ; \qquad k_5<7\times10^{-16}.$$

The values for k are systematically smaller in comparison with those from a previously published study. Possible reasons for the discrepancies have been investigated.

We decided to investigate the reactions of some diatomic molecules with ground-state phosphorus atoms produced in a discharge–flow system. The motivation for this investigation was to develop clean sources of phosphorus-containing radicals, including PO, PN and PCl, for study by laser-induced fluorescence.[1] However, apart from a major series of studies by Husain and coworkers,[2–5] there are relatively few publications dealing with reactions of the phosphorus atom in either the ground or excited states. Walsh[6] observed β and γ band emission of PO in a phosphorus glow, and proposed the mechanism

$$P(^4S)+O(^3P)+PO(X\,^2\Pi) \rightarrow PO(X\,^2\Pi)+PO^*(A\,^2\Sigma^+ \text{ or } B\,^2\Pi).$$

Later Davies and Thrush[7] studied the stoichiometry and chemiluminescence of the reaction of atomic oxygen with phosphorus, and concluded that the role of P atoms in the reaction $O+P_4$, giving PO* emissions, is probably minor.

Husain and coworkers[2,3] have published two studies of ground-state phosphorus atom reactions. They used both resonance absorption,[2] and the more sensitive resonance-fluorescence techniques[3] in the time-resolved mode. Husain *et al.* also studied the kinetics of excited states of phosphorus atoms[4,5] using resonance absorption.

Resonance fluorescence in a discharge–flow system is more sensitive than resonance absorption for detecting $H(^2S)$, $N(^4S)$ or $O(^3P)$.[8] In addition, detection of resonance fluorescence with wavelength resolution is routinely carried out, which is impossible in most flash-photolysis experiments. Wavelength resolution is especially desirable in the unequivocal identification of the absorbing atom in chemically complex systems. We have applied this technique to kinetic studies of phosphorus atoms, P(^4S). A comparison of kinetic data for phosphorus and nitrogen atoms, which have been studied extensively, should provide useful information concerning the relationship between reactivity and electronic structure.

In the present work, phosphorus atoms were generated principally by a microwave discharge in helium containing a trace of phosphorus trichloride. Phosphorus tribromide and phosphine were tested as alternative sources of P, but we found that phosphine is not suitable as a source of P atoms, presumably because of fast reactions between H atoms and radical fragments.

Two intense resonance fluorescence triplet lines are expected[8] for P atoms, *viz.* $P[3p^2\,4s(^4P_{1/2,3/2,5/2})] \rightarrow P[3p^3(^4S_{3/2})]$ ($\lambda = 178.77$, 178.29, 177.50 nm) and $P[3s\,3p^4(^4P_{5/2,3/2,1/2})] \rightarrow P[3p^3(^4S_{3/2})]$ ($\lambda = 167.97$, 167.46, 167.17 nm). However, in fact only the former triplet was usable, and the latter transition evidently is much weaker than indicated in the NBS Tables[9] (*vide infra*). All experiments were performed in systems where the concentration of P atoms was directly proportional to the intensity of resonance fluorescence. This concentration is $<1\times10^{12}$ cm^{-3} of undissociated PCl_3, *i.e.* $<4\times10^{10}$ cm^{-3} of P atoms. By comparison, reactions of phosphorus atoms P(^4S) have been studied by Husain and Slater, using the time-resolved resonance-fluorescence technique as described above.[3] They generated P atoms by photolysis of relatively large concentrations of PCl_3 (*ca.* 10^{14} cm^{-3}) at $\lambda > 160$ nm. However, our results gave systematically lower rate constants than those of Husain *et al.*,[2,3] but the differences cannot be explained adequately by differences in experimental conditions. There is a need for further independent work to resolve this problem.

EXPERIMENTAL

The experimental arrangement, based on that described in detail by Cheah *et al.*,[10] is summarised here. The monochromator was a large-aperture 1.5 m Fastie instrument (Jarrell-Ash 75-100), with a grating having 1200 lines per mm, blazed in 1st order at 500 nm. One of the two exit slits was used for 1st- and 2nd-order diffractions, while the other was used for 3rd and 4th orders, allowing photometric measurements from 115 to 800 nm. For detection of vacuum-u.v. radiation, a solar-blind photomultiplier (CsI cathode, EMR-541G-08-18) was used in conjunction with the second exit slit. Dark counts were negligible (<1 count s^{-1}). Dispersion at the exit slit was sufficient that the nitrogen-atom triplet transition (^4P–^4S) could be easily resolved ($\Delta\lambda \approx 50$ pm at 120 nm). The signals were input to an amplifier–discriminator, and counted with a fast-response (10 ns) photon-counting system. For wavelengths >180 nm, either a different solar-blind photomultiplier at 293 K (CsTe cathode, EMI 9705QB) or a thermoelectrically cooled photomultiplier (GaAs cathode, RCA C31034) was used.

To the resonance-fluorescence cell, which was constructed from a cuboid brass block and coated internally with Teflon, was attached a MgF_2 window. The block was fixed to the entrance slit of the spectrometer. O-rings were used for all seals. Flowing-type lamps which carried sealed-on MgF_2 windows were sealed into the brass block with double O-rings. The flow tube (Pyrex, 26 mm i.d.) passed through the brass block and was provided with four 25 mm holes directly opposite the MgF_2 windows. The tube had eight inlet jets for kinetic measurements, and was evacuated continuously, giving a maximum linear velocity of 1600 cm s^{-1}. Total pressure was determined with a calibrated capacitance manometer (Baratron model 222). Flows were determined with transducer flow meters (Hastings and

Brooks), as well as with a silicone-oil capillary flowmeter. Manufacturers' calibrations of flowmeters were checked.

Ground-state N(^4S), O(^3P) and P(^4S) atoms were produced by a 2.45 GHz discharge in a flow of 0.02–0.5 mol% N_2, O_2, PCl_3 and PBr_3 in helium (B.O.C. Ltd). Helium was purified with two molecular-sieve traps in series at 77 K. N_2 and O_2 were purified with molecular-sieve traps at 77 and 198 K, respectively. PCl_3 and PBr_3 (both from Hopkins and Williams) were thoroughly degassed and purified by repeated fractional distillation from 250 K (PCl_3) or 256 K (PBr_3) to 77 K. To form oxygen atoms, O(^3P), that were free of O_2, the reaction $N+NO \rightarrow N_2+O$, with [N] ≫ [NO], was used. NO was purified by passage through double cold fingers surrounded by n-propanol slush (153 K). Cl_2 was redistilled from a cylinder sample (Air Products 99.9%). NO_2 was produced using purified NO and O_2 and was purified by distillation using a slush bath at 195 K.

The resonance lamps were created by a microwave-excited atomic flow in which the concentrations of constituents were adjusted to produce a compromise between minimum scattered light and maximum fluorescence flux through the MgF_2 window. Addition of trace of N_2, O_2 or PCl_3 into the helium flow of the lamp yielded as exciting wavelengths the triplet at 120 nm for N(^4S), the triplet at 130.3 nm for O(^3P), and the triplets at 167.0 and 178.5 nm for P(^4S) atoms, respectively. With N_2 or O_2 as trace gases, the lamps were usable for over six months. However, when PCl_3 was used, the MgF_2 window had to be replaced regularly, owing to deposition of phosphorus polymers.

RESULTS AND DISCUSSION

P(^4S) ATOMIC RESONANCE FLUORESCENCE

Two strong transitions from the ground state of P[$3p^3(^4S_{3/2})$] and the excited states, P[$3p^24s(^4P_{1/2,3/2,5/2})$] and P[$3s3p^4(^4P_{5/2,3/2,1/2})$], are expected at wavelengths of 178.77, 178.29 and 177.50 nm and at 167.97, 167.46 and 167.17 nm, respectively.[9] The spectrum of our P atom microwave-excited lamp contained these two triplet emissions, as well as several lines of the chlorine atom, as shown in fig. 1(*a*) and (*b*).

However, the atomic resonance fluorescence of P atoms excited with this lamp consisted of only the one triplet centred at 178 nm. It follows that the oscillator strength of the transition of the other (non-observed) triplet at 167 nm is much smaller than that given in the NBS Tables,[9] by at least one order of magnitude. In fact, the NBS value of $f = 1.4$ for the 167.8 nm triplet is based on theoretical work that neglects configuration interaction.[12]

According to the compilers of the NBS Tables, this theoretical value is uncertain and likely to be too high.[9] The present work provides direct evidence in support of this view. Certainly the analogous N(^4S) atom shows a much higher f-value for its $2p^23s$–$2p^3$ triplet ($f = 0.35$)[9] than for its $2s2p^4$–$2p^3$ triplet ($f = 0.13$).

The f-value for the $3p^24s$–$3p^3$ triplet of P at 178 nm is stated to be 0.31,[9] based on reasonably reliable data of Lawrence.[13] In view of this large magnitude of the f-value, detection of P(^4S) atoms by atomic resonance should be extremely sensitive, and comparable in this respect with the detection of N(^4S) atoms. In addition, the longer wavelength of detection of P(^4S) at 178 nm, compared with that of N(^4S) at 120 nm, is favourable for experimental reasons.

In fact, resonance fluorescence of P(^4S) atoms readily was observed using a discharge in He + PCl_3 as the source. A curve-of-growth relating the resonance fluorescence intensity, I_F, of phosphorus atoms to the PCl_3 concentration for the triplet transition of P at 178 nm is shown in fig. 2. I_F has been normalized to the intensity of the scattered light (I_S) at the wavelength of the transition; I_S is

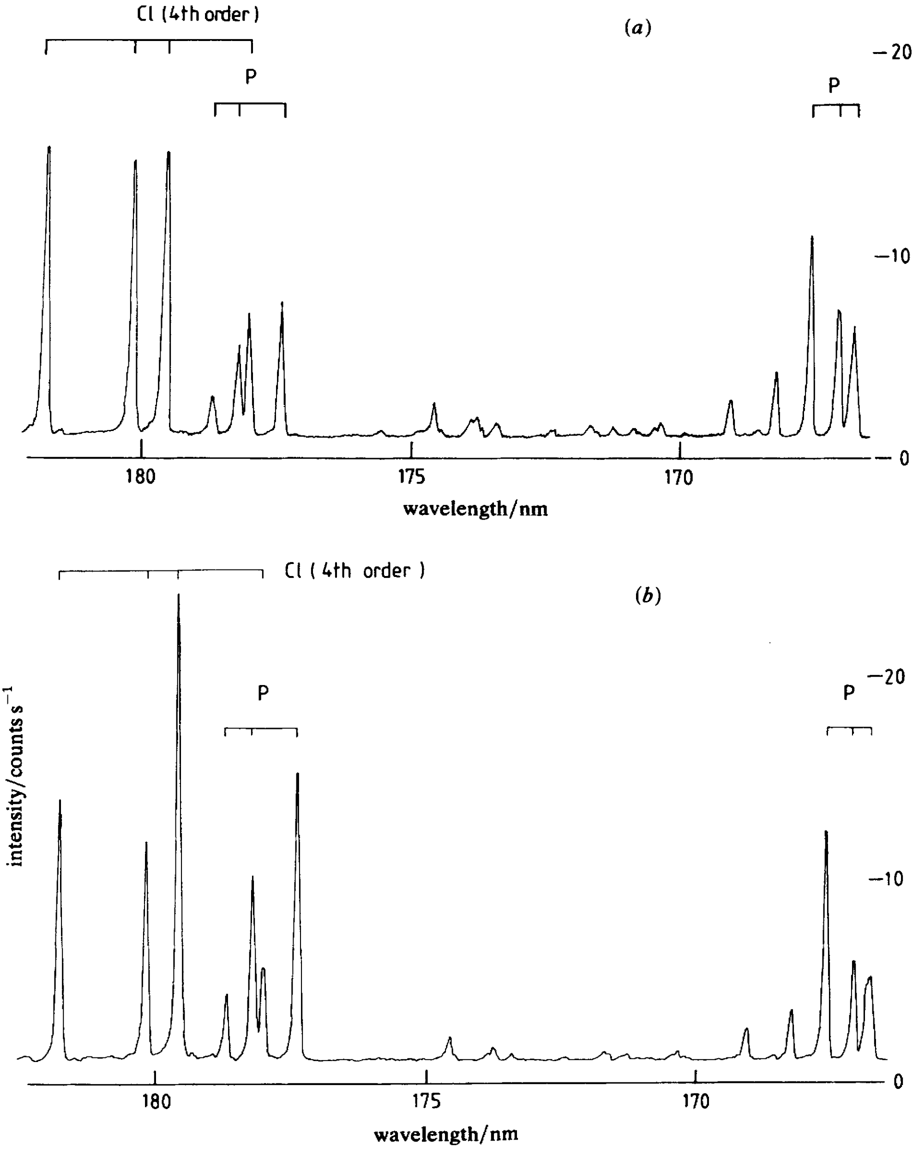

FIG. 1.—(*a*) Resolved spectrum from the P atom resonance lamp, observed in scattered light. (*b*) Resolved fluorescence spectrum of P(^4S) atoms, including scattered light. 3rd-order spectra. The lines of Cl are in the 4th order; therefore their wavelengths must be multiplied by 3/4 of scale reading (*i.e.* 134–137 nm).

proportional to I_0, the intensity of incident light. The curve of fig. 2 shows that the linear range of dependence of I_F upon [PCl_3] extends up to a concentration of 1×10^{12} cm^{-3}. The concentration of P atoms formed clearly is much lower than that of undissociated PCl_3 (see below).

For pseudo-first-order kinetic analysis of the reaction of P atoms with molecule XB

$$P(^4S)+XB \rightarrow PX+B$$

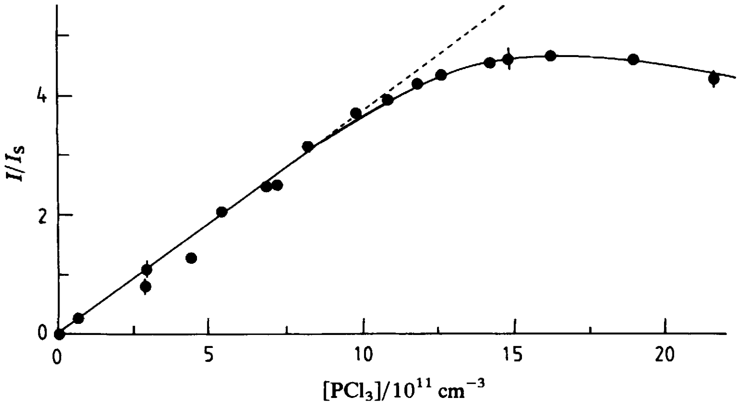

FIG. 2.—Variation of the fluorescence intensity of P atoms at the 175.5 nm line with undissociated PCl_3 concentration. I = fluorescence intensity, I_S = scattered light intensity.

it is required that $[P] \ll [XB]$. Therefore, it should be verified that for concentrations of P lying within the linear region of the plot of I_F/I_S against $[PCl_3]$ these concentrations are much less than the concentrations of XB to be used (10^{13}–10^{15} cm^{-3}). Consequently, a measurement of the P atom concentration was made using the $P+O_2$ reaction

$$P(^4S)+O_2 \rightarrow PO+O(^3P).$$

The rate constant for this reaction is relatively small (*ca.* 10^{-13} cm^3 molecule^{-1} s^{-1} at 293 K), but quantitative conversion of P atoms to O atoms could be achieved by using a high concentration of O_2. A curve-of-growth of the intensity of fluorescence of $P(^4S)$ atoms was constructed, as a function of $O(^3P)$ atom fluorescence intensity at 130.5 nm. In addition, a curve-of-growth relating $O(^3P)$ atom fluorescence intensity to [O], using the titration reaction

$$N+NO \rightarrow N_2+O(^3P)$$

was determined. In this way, the curve-of-growth relating P atom fluorescence intensity to [P] was obtained; the result is shown in fig. 3. The uncertainty of the data is relatively high because $O(^3P)$ atom fluorescence intensity is much weaker

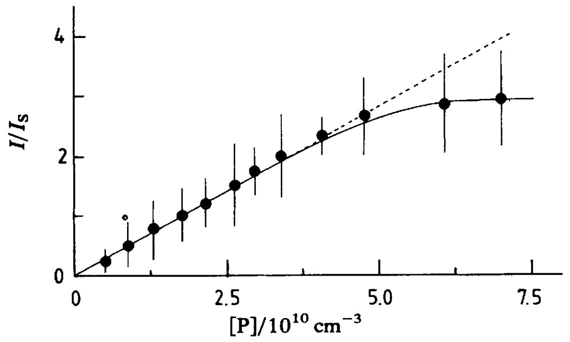

FIG. 3.—Curve-of-growth for P atom resonance fluorescence at the 175.5 nm line. Calibration of [P] from the $P+O_2 \rightarrow PO+O$ reaction (see text).

than $P(^4S)$ atom fluorescence intensity. However, a linear relation between I_F and [P] was found to extend up to $[P] = 5 \times 10^{10}$ cm^{-3}. As shown by comparison of fig. 2 and 3, this upper limit value for [P] was obtained from dissociation of a concentration of PCl_3 equal to *ca.* 1.25×10^{12} cm^{-3}. We conclude that the mean yield of P atoms from PCl_3 molecules by a microwave discharge under the present experimental conditions was *ca.* 4%.

The range of linear dependence of I_F and [P] found experimentally in this work agrees with that calculated by Husain and Slater[3] for higher total bath-gas concentrations (*ca.* 6.5×10^{17} cm^{-3}), where Lorentz broadening is not negligible. The data of fig. 3 may be compared with the calculated lines shown in fig. 9(*d*)–(*f*) of ref. (3).

KINETIC STUDIES

N + NO REACTION KINETICS

As a check on the flow system and its calibrations, we measured initially the rate constant for the well-studied reaction

$$N(^4S) + NO \rightarrow N_2 + O(^3P)$$

according to the technique described previously.[10] The obtained value for k at 298 K was $(2.8 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, in good agreement with previous measurements.[10] Details of the present investigation will be presented elsewhere.[11]

KINETICS OF REACTIONS $P(^4S) + XB$

In order to work within the linear range of dependence of I_F upon [P], the initial concentration of [P] was set $\leqslant 5 \times 10^{10}$ cm^{-3}. The sensitivity of detection of P atoms was sufficient for a twenty-fold reduction in [P] to be monitored; this corresponds to detection of 3×10^9 cm^{-3} with a signal-to-noise ratio of unity.

For the reaction

$$P(^4S) + XB \xrightarrow{k} PX + B$$

pseudo-first-order kinetic analysis may be employed when XB is in large excess, $[XB] \gg [P]$. The simplest case is when concomitant first-order wall removal of atoms is either negligible or is unaffected by addition of reagent XB. When analysis based on a fixed observation point is used, the appropriate integrated rate expression is eqn (I)[14–16]

$$\ln([P]_0/[P]) = k[XB]t. \qquad \text{(I)}$$

In eqn (I), $[P]_0$ and [P] are the concentrations of phosphorus atoms at the observation point in the absence and presence of XB. Analysis according to eqn (I) normally is suitable for the study of reactions possessing large rate constants, in excess of 10^{-12} or 10^{-13} cm^3 molecule^{-1} s^{-1}, as for example the $P + NO_2$ reaction studied in the present work.

When the reaction under study is extremely slow, *e.g.* the P + NO reaction with $k_4 = 3.4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (see below), wall loss of atoms, k_w, may be as fast as or faster than the reaction. In such a case, eqn (I) is still valid if k_w is independent of [XB]. However, an alteration in k_w to a new value k'_w, caused by addition of XB, can affect the observed kinetics. Simple analysis then gives the modified rate equation eqn (I′)[14–16]

$$\ln([P]_0/[P]) = k[XB]t + (k_w - k'_w)t. \qquad \text{(I′)}$$

The pseudo-first-order rate constant, k_{obs}, which is equal to the slope of a plot of ln ($[P]_0/[P]$) against time, is then given by eqn (II)

$$k_{obs} = k[XB] + (k_w - k'_w). \tag{II}$$

Plots of k_{obs} against [XB] should yield straight lines with slopes k, and intercepts which may be non-zero, depending on the magnitude of $(k_w - k'_w)$.

It is not feasible with the fixed observation point method directly to determine k_w absolutely. However, an estimate of k_w was obtained by comparing values of $[P]_0$ as a function of flow velocity at constant flow-tube pressure. Variation of flow velocity changes the elapsed time between the source of P atoms (in the discharge) and the observation point. Experiments of this type indicated a value of 45 s^{-1} for k_w, with error limits conservatively estimated as ±50%.

Corrections to kinetic data obtained with the discharge–flow method have been discussed elsewhere.[8] In summary, no corrections were needed in the present work to allow for axial pressure gradient along the flow tube nor for radial diffusion.

However, a small correction was needed for axial diffusion, according to eqn (III)[17]

$$k' = k_{obs}[1 + (k_{obs} + 2k_w)D/v^2] \tag{III}$$

where k' is the corrected pseudo-first-order rate constant, D is the diffusion coefficient of P atoms, and v is the flow velocity. For the usual flow velocity of 1600 cm s^{-1} and at 1.2 Torr,† the corresponding value of k'/k_{obs} was $1.016 + 1.7 \times 10^{-4}\, k_{obs}$ using $D = 445$ cm^2 s^{-1} at 293 K. The range of k_{obs} included a maximum value of 600 s^{-1} for the rapid $P + NO_2$ reaction, down to values of <50 s^{-1} typical of the slower $P + Cl_2$ and $P + O_2$ reactions. Thus the maximum correction for axial diffusion was 11% for a few of the faster $P + NO_2$ data, with 3% being a typical magnitude for most of the other results. A few data on the slow P + NO reaction were obtained with the lower flow velocity of 890 cm s^{-1}; in these cases the value of k'/k_{obs} was $1.052 + 5.7 \times 10^{-4}\, k_{obs}$, giving a constant correction of 5% for the range of k_{obs} that was measured.

The data reported in the following sections have incorporated the small axial diffusion correction, and in the case of the $P + NO_2$ reaction allowance to the flow rate was made to allow for partial dimerization of NO_2 in the reservoir volume.[18]

THE $P + NO_2$ REACTION

Fig. 4(*a*) shows typical data for the rapid depletion of $P(^4S)$ atoms in the presence of NO_2. Satisfactory first-order plots of ln ($[P]_0/[P]$) were obtained over at least three lifetimes, using values of $[NO_2]_0/[P]_0$ in the range 46–630. A typical initial P atom concentration was 3×10^{10} cm^{-3}. No significant ordinate intercepts were observed for the first-order plots.

Fig. 4(*b*) shows a summary of the data, in the form of a plot of k' against $[NO_2]$ in the concentration range $3.14 \times 10^{13} \geqslant [NO_2]_0/\text{cm}^{-3} \geqslant 2.30 \times 10^{12}$. Full circles in fig. 4(*b*) show data obtained using a discharge in $He + PCl_3$ as the source of P atoms, whilst open circles show data using $He + PBr_3$ as the source. The results from PBr_3 were fewer and more scattered than the data from PCl_3, since the yield of P atoms from PBr_3 was lower than that from PCl_3, mainly because of the low

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† 1 Torr = 101 325/760 Pa.

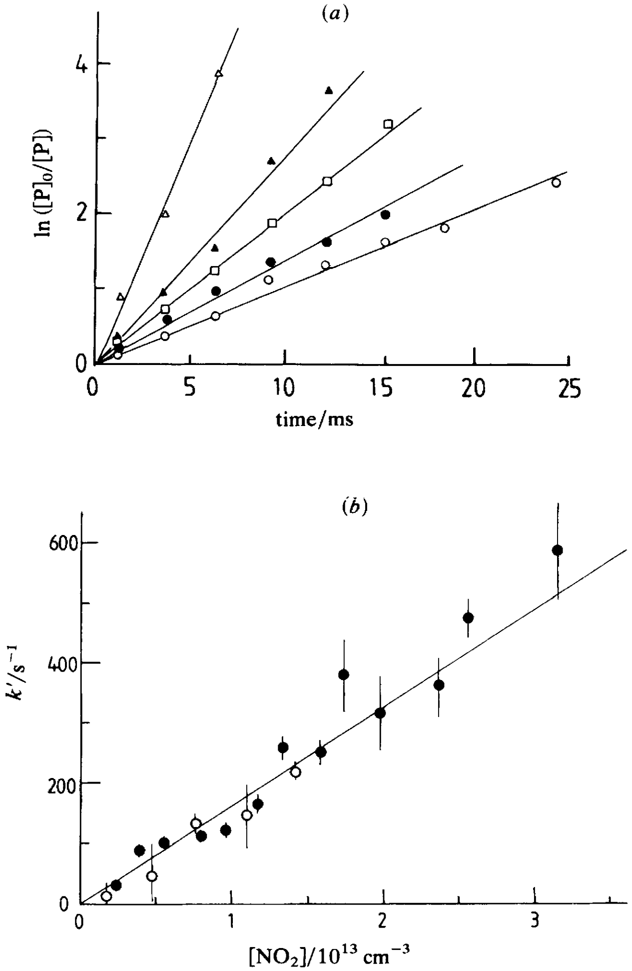


FIG. 4.—Kinetics of the reaction $P(^4S)+NO_2$ at 293 K. (*a*) Typical first-order logarithmic plots for P atom decay. $NO_2/10^{13}\ cm^{-3}$ as follows: △, 3.15; ▲, 1.57; □, 1.18; ●, 0.79; ○, 0.39. (*b*) Summary plot for the variation of the pseudo-first-order rate constant k' with $[NO_2]$. Source of P atoms: ●, PCl_3; ○, PBr_3.

vapour pressure of PBr_3. However, values of the rate constant k_1 (1σ) obtained from PCl_3 and PBr_3 were essentially identical, being $(1.62\pm0.07)\times10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$ and $(1.64\pm0.20)\times10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$, respectively. (A discharge in $He+PH_3$ was investigated as a possible source of P atoms, but none could be detected.)

Resonance fluorescence at 134.7 nm showed that Cl atoms persisted, under some conditions, beyond the $He+PCl_3$ discharge as far as the observation point. After the flow tube had been used for some time, the Cl atoms were found gradually to disappear on the walls. However, no difference in P atom kinetics could be detected, whether or not Cl atoms persisted into the reaction zone. This result is in agreement with the finding that substitution of PCl_3 by PBr_3 as the source of P atoms had no effect on the $P+NO_2$ or $P+O_2$ reactions (see below).

REACTIONS $O+PCl_3$, PCl_2, PCl

We investigated further the possible interference with our P atom kinetic studies of radical fragments (such as PCl_2, PCl) formed in the discharge of $He+PCl_3$. It was not possible directly to detect PCl_2 or PCl radicals by resonance radiation. However, the effects of these species (if formed) were examined by introducing a stream of $O(^3P)$ atoms into a flow of P atoms, or of undissociated PCl_3+He. $O(^3P)$ atoms ($\leqslant 3\times10^{13}$ cm^{-3}) were generated from $N(^4S)$ atoms by means of the N+NO reaction. As shown in fig. 5(*a*), P atoms were not attenuated by addition of O atoms, up to a concentration of O atoms of at least 2.7×10^{13} cm^{-3}. However, the O atom concentration was depleted, and a greater depletion was seen with the discharge off. This result [fig. 5(*b*)] indicates that O atoms react more rapidly with undissociated PCl_3 than with any PCl_2 and PCl radical fragments formed by the discharge. An approximate estimate gave a value of *ca.* 1.2×10^{-11} cm^3 molecule^{-1} s^{-1} for the rate constant of the $O+PCl_3$ reaction.

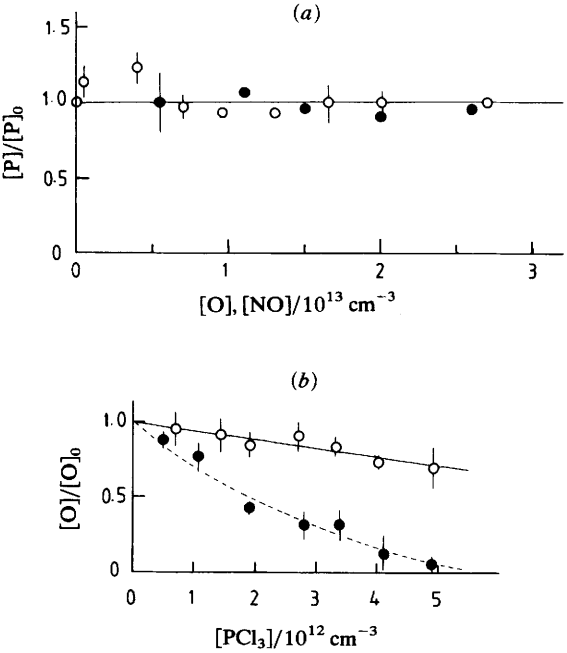


FIG. 5.—(*a*) Variation of the concentration of $P(^4S)$ with added $[O(^3P)]$. Note: no depletion of P atoms could be observed. ○, For the reaction $P(^4S)+O(^3P)$; ●, for the reaction $P(^4S)+NO$. (*b*) Depletion of the concentration of $O(^3P)$ as a function of $[P(^4S)]$. ○, For the reaction $O(^3P)+PCl_3$; ●, for the reaction $O(^3P)+P(^4S)+$undissociated PCl_3+dissociation fragments.

The above results indicate that the present very dilute P atom source should be satisfactory for kinetic studies, and not involve any side reactions due to radical fragments formed by the discharge.

THE $P+O_2$ REACTION

As for the $P+NO_2$ reaction, satisfactory pseudo-first-order kinetic plots were obtained for the $P+O_2$ reaction. However, the rate of the $P+O_2$ reaction was considerably slower, and O_2 concentrations were greater than those of NO_2, being in the range $5.0\times10^{14}\geqslant[O_2]/cm^{-3}\geqslant3.2\times10^{13}$ with $[O_2]/[P]\geqslant640$. Fig. 6 shows a summary of the data in the form of a plot of k' against $[O_2]$. As for the $P+NO_2$ reaction, linear regression analysis showed no significant ordinate intercept for the plot of k' against $[O_2]$. The mean value of k_2 found for the $P+O_2$ reaction was $(9.8\pm0.2)\times10^{-14}$ cm^3 molecule^{-1} s^{-1}, using $He+PCl_3$ as the source of P atoms. Several results using $He+PBr_3$ as the source of P atoms gave a similar value of $(9.6\pm0.5)\times10^{-13}$ cm^3 molecule^{-1} s^{-1}.

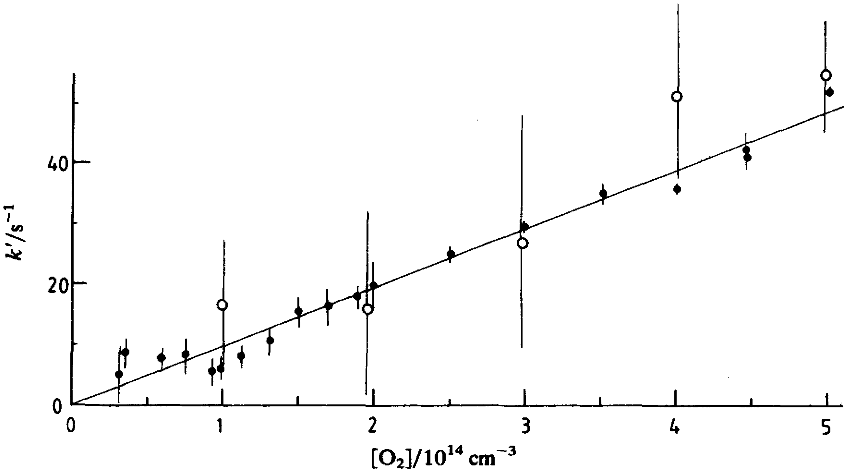


FIG. 6.—Kinetics of the reaction $P(^4S)+O_2$ at 293 K. Summary plot for the variation of the pseudo-first-order rate constant k' with $[O_2]$. Source of P atoms: ●, PCl_3; ○, PBr_3.

THE $P+Cl_2$ REACTION

The rate of the $P+Cl_2$ reaction was found to be intermediate between that of the $P+NO_2$ and $P+O_2$ reaction. As before, plots of ln $([P]_0/[P])$ against time were linear, using Cl_2 concentrations in the range $2.37\times10^{14}\geqslant[Cl_2]/cm^{-3}\geqslant1.2\times10^{13}$, with $[Cl_2]/[P]\geqslant240$. Fig. 7 shows a summary of the data in the form of a plot of

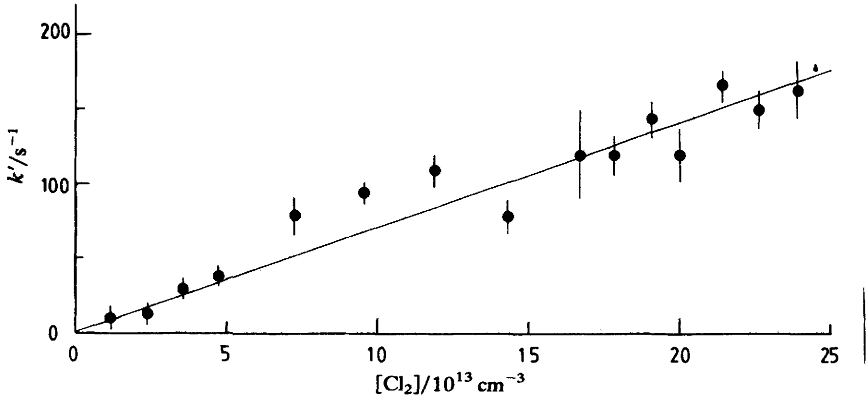
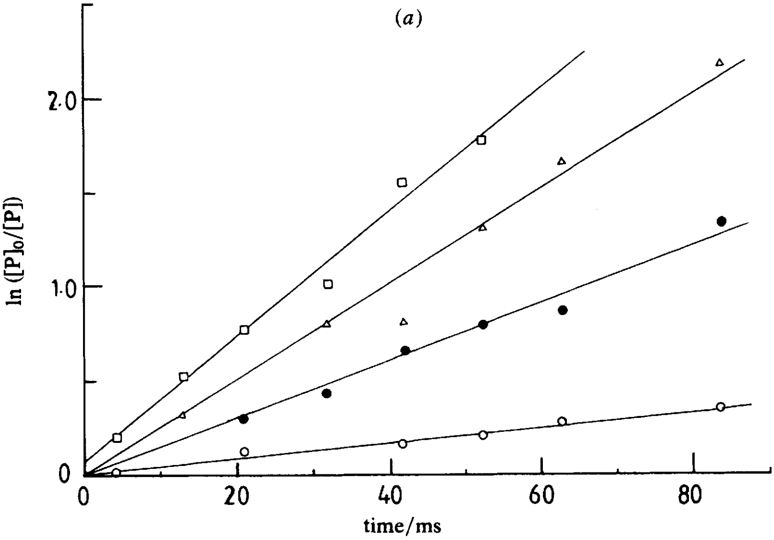


FIG. 7.—Kinetics of the reaction $P(^4S)+Cl_2$ at 293 K. Summary plot for the variation of the pseudo-first-order rate constant k' with $[Cl_2]$.

k' against $[Cl_2]$; no significant ordinate intercept was shown. Using He + PCl_3 as the source of P atoms, the mean value of the rate constant k_3 for the P + Cl_2 reaction was $(7.0 \pm 0.4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

THE P + NO REACTION

Reaction of P atoms with nitric oxide was found to be slower than any of the elementary reactions studied above. Therefore, a lower flow velocity (890 cm s^{-1}) was employed for the P + NO study, in order to give appreciable decays of [P]. Fig. 8(*a*) shows typical pseudo-first-order decay plots for the P + NO reaction, giving satisfactory linear correlations over two lifetimes. The range of nitric oxide concentrations was $1.65 \times 10^{15} \geq [NO]/cm^{-3} \geq 2.5 \times 10^{14}$. The data for the P + NO



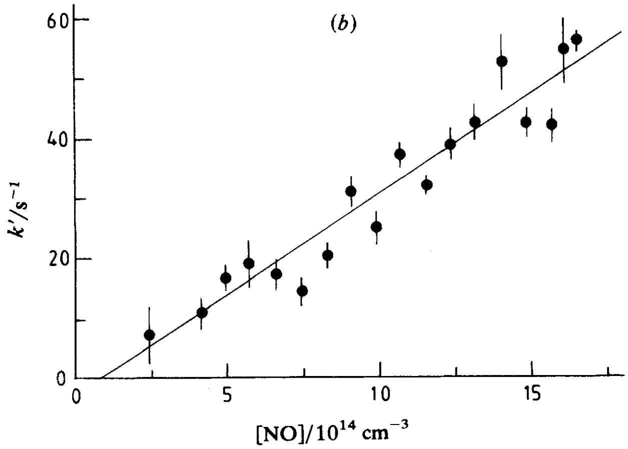


FIG. 8.—Kinetics of the reaction $P(^4S)$ + NO at 293 K. (*a*) Typical first-order logarithmic plots for P atom decay $[NO]/10^{14}$ cm^{-3} as follows: □, 10.7; △, 9.9; ●, 7.4; ○, 2.5. (*b*) Summary plot for the variation of the pseudo-first-order rate constant k' with [NO].

reaction are summarised in fig. 8(*b*), which indicates the small magnitudes of k' that were measured, namely 7-56 s^{-1}. Fig. 8(*b*) shows a significant ordinate intercept of $-3\ s^{-1}$, which can be equated to the term $(k_w - k'_w)$ in eqn (I′). The mean value of k_4 for the P+NO reaction was $(3.4 \pm 0.1) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}.

The ratio at 293 K of rate constants (k_1/k_4) for the $P+NO_2$ and P+NO reactions was determined to be 480. Therefore, the measured rate of the P+NO reaction was extremely sensitive to a trace of NO_2 impurity in the NO. In the present work, repeated purifications of nitric oxide were carried out, until an essentially constant value for k_4 was obtained. However, we did not have available a method for measuring *ca.* 0.1 mol % or less of NO_2 in NO, so that the present rate constant for P+NO must be regarded strictly as an upper limit, $k_4 \leqslant 3.4 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}.

Out of the P atom reactions studied, the P+NO reaction is the only one that is conceivably slow enough to be third order, *i.e.*

$$P + NO + M \xrightarrow{k_{4,M}} PNO + M.$$

At the experimental total pressure of 1.2 Torr (M = He), the value of the third-order rate constant $k_{4,M}$ would be 8.9×10^{-31} cm^6 $molecule^{-2}$ s^{-1}, corresponding to $k_4 = 3.4 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}. In order to investigate the possible dependence upon third-body concentration [M], k_4 was measured over the range $5.5 \times 10^{16} \geqslant [He]/cm^{-3} \geqslant 2.9 \times 10^{16}$. No significant variation in k_4 could be detected, thus indicating that the P+NO reaction was a second-order bimolecular process, under the conditions used. It was not feasible to extend the present kinetic study to He concentrations above 5.5×10^{16} cm^{-3}, because of experimental constraints.

THE $P + PCl_3$ REACTION

The reaction of $P(^4S)$ atoms with PCl_3, which has been reported by Husain and Slater[2] to have a rate constant of $(1.7 \pm 0.3) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 293 K, was examined. However, under no conditions were we able to observe any depletion of $P(^4S)$ atoms in the presence of phosphorus trichloride using $[PCl_3] \leqslant 1.5 \times 10^{15}$ cm^{-3} and reaction times up to 70 ms. Based on these results, an upper limit for the rate constant k_5 for the $P+PCl_3$ reaction was determined to be $\leqslant 7 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}.

METASTABLE EXCITED $P(^2D, {}^2P)$ ATOMS

Excited $P(^2D, {}^2P)$ atoms were found by Husain and coworkers[4,5] to be formed in the photolysis of PCl_3. Therefore we determined to investigate whether these excited atoms were present in our discharge-flow source of P atoms. A microwave discharge in N_2, diluted with Ar or He, is known to generate appreciable concentrations of metastable $N(^2D)$ atoms. In the present work, detection of $P(^2D, {}^2P)$ atoms was attempted using the 185.9 nm and 254.1 and 214.0 nm lines, which should be extremely sensitive in resonance fluorescence. However, no fluorescence could be detected; it is concluded that excited $P(^2D, {}^2P)$ atoms, if formed, were rapidly relaxed to the ground $P(^4S)$ state, before reaching the reaction zone.

DISCUSSION

COMPARISON WITH PREVIOUS WORK

Table 1 shows a summary of elementary reaction rates of $P(^4S)$ atoms that have been studied in the present work by resonance fluorescence in a discharge-flow

TABLE 1.—RATE CONSTANTS (cm^3 $molecule^{-1}$ s^{-1}) FOR P ATOM REACTIONS AT 293 K

	this work	ref. (3)	ref. (2)
O_2	$(9.9 \pm 0.2) \times 10^{-14}$	$(2.1 \pm 0.3) \times 10^{-12}$	$(2.0 \pm 0.1) \times 10^{-12}$
NO_2	$(1.62 \pm 0.07) \times 10^{-11}$	—	—
Cl_2	$(7.0 \pm 0.4 \times 10^{-13}$	$(3.4 \pm 0.3) \times 10^{-12}$	$(3.9 \pm 0.05) \times 10^{-12}$
NO	$(3.4 \pm 0.1) \times 10^{-14}$	$(5.3 \pm 0.5) \times 10^{-13}$	$(4.3 \pm 0.1) \times 10^{-13}$
PCl_3	$< 7 \times 10^{-16}$	$(1.7 \pm 0.3) \times 10^{-12}$	$(2.5 \pm 0.05) \times 10^{-11}$

system. Also shown are the rate constants measured by Husain *et al.* using resonance absorption[2] and resonance fluorescence,[3] coupled to a flash-photolysis apparatus. Surprisingly, there is no agreement between the present and previous resonance-fluorescence data; the present values for the rate constants of $P(^4S)$ atoms with O_2, Cl_2, NO and PCl_3 all are much less than those reported previously, by factors varying from $>2 \times 10^3$ for $P + PCl_3$ to 4.9 for $P + Cl_2$. Kinetic data for the $P + NO_2$ reaction have not been obtained hitherto.

In comparing flash-photolysis results from resonance absorption[2] and resonance fluorescence,[3] Husain and Slater[3] have divided the phosphorus atom reactions studied into two groups: (*a*) reactions of diatomic molecules and (*b*) reactions of polyatomic molecules. The rate constants[2,3] at 293 K for group (*a*) showed good agreement, when account was taken of the non-unitary value of γ (0.51) in the pseudo-Beer–Lambert expression employed in the resonance absorption work.[3] On the other hand, the rate constants for group (*b*) showed poor agreement, with resonance-fluorescence values[3] being considerably smaller than those from resonance absorption.[2] These major differences were attributed[3] to extensive short-wavelength photolysis of the substrate polyatomic molecules, including PCl_3 and hydrocarbons, in the resonance-fluorescence work.[3]

The present rate constants for reactions of P atoms with diatomics are all considerably smaller than those reported by Husain and Slater.[3] In addition, no reaction between P atoms and the polyatomic PCl_3 was observed by us, whilst Husain and Slater[3] reported a value of $(1.7 \pm 0.3) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. A major difference between the present and previous[2,3] work is the relatively large concentrations (*ca.* 10^{14} cm^{-3}) of PCl_3, and hence of dissociation products, in the previous work.[2,3] The maximum PCl_3 concentration dissociated in the present work was 2×10^{12} cm^{-3}, and we have shown that dissociation products from such low concentrations have no influence on the kinetics of the P atom reactions which were studied. It appears that the yield of P atoms from PCl_3 is much greater using a microwave discharge than from short-wavelength photolysis. This is not surprising, in view of the higher energy available from the discharge.

The consequence is that the concentration of P atoms, relative to other dissociation products, may be expected to be much smaller in the flash-photolysis experiments than in the discharge–flow studies. As found directly in the present work using a discharge, chlorine atoms can be expected to be a major product of photolytic dissociation of PCl_3. Molecular chlorine also is likely to be a major product of photolytic dissociation. A possible explanation of the apparent reaction of P with PCl_3 reported by Husain *et al.*[2,3] can be advanced. If the yield of Cl_2 from PCl_3 is appreciable, the observed depletion of P atoms, following the flash photolysis of PCl_3, is to be assigned to reaction of P atoms with photolytically generated Cl_2. This hypothesis is consistent with the observation by Husain and Slater[3] of a larger rate constant for the $P+Cl_2$ reaction than the apparent rate constant for the $P+PCl_3$ reaction, since ($[Cl_2]$ formed) < ($[PCl_3]$ initial).

We feel that photolysis products of PCl_3 may have influenced also the kinetics of the P atom+diatomic reactions studied previously.[2,3] A tentative explanation for high values of the $P+Cl_2$, $P+O_2$ and $P+NO$ rate constants[3] can be based on the photolytic production of major amounts of Cl atoms from PCl_3. Addition of Cl_2, O_2 or NO may then lead to accelerated recombination of Cl atoms, *via* $Cl+Cl+M \rightarrow Cl_2+M$, or $Cl+NO(O_2)+M \rightarrow ClNO+M$ followed by $Cl+ClNO \rightarrow Cl_2+NO$. Molecular Cl_2, reaction of P atoms with which has the largest rate constant reported by Husain and Slater,[4] is known to be particularly efficient as a third-body M in the $Cl+Cl+M$ reaction. Thus, recombination of Cl atoms promoted by addition of the diatomic molecular substrate XB could produce increased amounts of Cl_2, giving a higher depletion rate of P atoms than is accounted for by the direct reaction $P+XB$. This mechanism also may apply to the $P+PCl_3$ results. A possible problem with this explanation for high rate constants in the flash-photolysis work is that the third-order rate constants for Cl atom recombination would appear to be too small under the conditions used[3] to account for all the extra Cl_2 that would have to be generated. However, the $Cl+NO+M$ reaction would be sufficiently fast in the $P+NO$ studies for this purpose. It remains to be considered whether other photolytically formed fragments such as PCl and PCl_2 could influence the P atom depletion rate in some manner. Unfortunately, relevant kinetic data on PCl and PCl_2 reactions are totally absent from the literature. Whatever the detailed mechanisms involved, it is clear that, in any future studies of P atom reactions, the use of low concentrations of PCl_3, in order to minimize dissociation products, is extremely desirable.

Several possible problems associated with the present discharge–flow studies of P atom reactions have been considered and set aside in preceding sections. Detection of wavelength-resolved fluorescence ensured that no species other than $P(^4S)$ atoms were being followed kinetically. Effects upon [P] of dissociation products of PCl_3 have been considered in detail, and found not to be important. No significant difference in P atom depletion rates was found when PBr_3 was substituted for PCl_3 as the source of P atoms. Surface removal of P atoms on the flow tube was found to be moderately rapid, with a first-order rate constant $k_w \approx 45\ s^{-1}$. However, only in the case of the very slow $P+NO$ reaction did the appropriate kinetic analysis reveal a measurable change in k_w consequent upon adding reactive substrate XB to the P atom flow. Thus it seems unlikely that the present work involves major systematic errors. If such errors are present nonetheless, the most likely source would be unexpectedly large wall loss of P atoms not revealed by the usual analysis.

COMPARISON OF P ATOM AND N ATOM RATE CONSTANTS

Although ground-state $P(^4S)$ and $N(^4S)$ atoms have similar electronic structures, the rate constants at 293 K for their analogous reactions show considerable differences. Some of these differences have been discussed by Husain and Norris,[2] whilst the relevant correlation diagrams connecting reactant and product states for certain $P+XB$ reactions have been presented by Acuna *et al.*[4] As pointed out previously,[2] the reaction of $N(^4S)+O_2$ is considerably slower than that of $P(^4S)+O_2$, whilst the converse is true for the $N(^4S)+NO$ and $P(^4S)+NO$ reactions. The present work confirms these conclusions.

The reactions of $P(^4S)$ atoms with NO_2 and with Cl_2 in both cases are found by us to be faster at 293 K than the analogous reactions of $N(^4S)$ atoms. Comparison of the $P+Cl_2$ and $N+Cl_2$ reactions is limited by the absence of reliable data on the $N+Cl_2$ reaction, although unpublished work by Clark[19] from this laboratory gives an upper limit of $\leqslant 1\times 10^{-13}$ cm^3 molecule^{-1} s^{-1} for the rate constant of this reaction.

The rate constant at 298 K for the $P+NO_2$ reaction is nearly an order of magnitude greater than that for the $N+NO_2$ reaction.[11,20] The slow rate of the $N+NO_2$ reaction may be correlated with the formation of N_2O+O as products[20] *via* the unusual attack of the N atom on the central (N) atom in NO_2. The rapidity of the $P+NO_2$ reaction, on the other hand, suggests a simple mechanism, leading to $PO+NO$ rather than to $PNO+O$ (or the less likely $PN+O_2$) as the reaction products.

PRODUCTION OF PX-TYPE RADICALS

The present work indicates that the reactions of P(^4S) atoms with NO_2, Cl_2, O_2 and NO all may be expected to lead to the relevant PX-type radicals. In the case of the $P+NO_2$ reaction, the dominant product channel is uncertain, although we have argued above that it probably occurs to give $PO+NO$. Thus PO radicals can be formed from $P+NO_2$ or $P+O_2$, PCl radicals from $P+Cl_2$, and PN radicals from $P+NO$. The reaction of P atoms with NO_2, certainly, and those of P atoms with O_2, Cl_2, probably, are fast enough to generate PX radicals efficiently from P atoms under typical flow conditions. The $P+NO$ reaction is rather slower, but may prove satisfactory for the formation of PN radicals. A limitation to the formation of PX radicals from $P+XB$ reactions is the maximum P-atom concentration that can be generated in a discharge–flow system. With the present source of P atoms, namely a discharge in PCl_3+He, this consideration limits [PX] to a value no greater than 6×10^{11} cm^{-3}, since ([PX] formed) $\leqslant$ ([P] consumed), and *ca.* 6×10^{11} cm^{-3} is the maximum concentration of P atoms that could be generated readily. However, concentrations of PX radicals of the order of 10^{11} cm^{-3} should be adequate for detection by laser-induced fluorescence, as shown by Clyne and Heaven[21] for PO radicals formed from the reaction of PH_3 with N and O atoms.

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