

ELECTRONICALLY EXCITED IODINE ATOMS,  $I(5p^5\ ^2P_{1/2})$ :  
A KINETIC STUDY OF SOME CHEMICAL REACTIONS BY ATOMIC  
ABSORPTION SPECTROSCOPY USING TIME-RESOLVED  
ATTENUATION OF RESONANCE RADIATION AT  $\lambda = 206.23\text{ nm}$   
{ $I[5p^46s(^2P_{3/2}) \leftarrow 5p^5(^2P^0_{1/2})]$ }

J. J. DEAKIN and D. HUSAIN

*Department of Physical Chemistry, University of Cambridge, Lensfield Road,  
Cambridge (Gt. Britain)*

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SUMMARY

Electronically excited iodine atoms,  $I(5p^5\ ^2P_{1/2})$ , 0.943 eV above the lower spin orbit level ( $J = 3/2$ ) of the  $5p^5$  ground state configuration, have been generated by the ultra-violet pulsed irradiation of  $CF_3I$  in the presence of excess helium buffer gas. The optically metastable atoms were monitored photoelectrically in absorption by time-resolved attenuation of atomic resonance radiation at  $\lambda = 206.23\text{ nm}$  { $I[5p^46s(^2P_{3/2}) \leftarrow 5p^5(^2P^0_{1/2})]$ }. The kinetic decay of the excited atoms in the presence of the added gases  $Cl_2$ ,  $Br_2$ ,  $ICl$ ,  $IBr$ ,  $NOCl$  and  $NOBr$  has been investigated in detail and second order rate constants for chemical reaction with these molecules are reported and compared with rate data obtained hitherto from plate photometry. Further, the temperature dependence of the reaction rate constants has been studied in the range 294–421 K, the results for the chemical reactions of  $I(5^2P_{1/2})$  with  $Cl_2$  and  $Br_2$  being most detailed. The Arrhenius parameters for these two reactions were found to be as follows:

	$\log_{10}A\ (\text{cm}^3\ \text{molecule}^{-1}\ \text{sec}^{-1})$	$E\ (\text{kcal mole}^{-1})$
$k_{Cl_2}$	$-11.6 \pm 0.2$	$1.6 \pm 0.3$
$k_{Br_2}$	$-10.4 \pm 0.2$	$0.4 \pm 0.3$

INTRODUCTION

Electronically excited iodine atoms,  $I(5p^5\ ^2P_{1/2})$ , 0.943 eV above the lower spin orbit level ( $^2P_{3/2}$ ) of the  $5p^5$  ground state configuration<sup>1</sup>, have been the object of a number of kinetic investigations by direct spectroscopic methods<sup>2</sup>. The majority of the rate data for this species have been derived by time-resolved atomic absorption spectroscopy on account of the high optical metastability of  $I(5^2P_{1/2})$ <sup>3,4</sup>, principally involving plate photometry following flash photolysis<sup>5-7</sup>. More recently<sup>8,9</sup>, we have described a method for monitoring these excited atoms in absorption by attenuation of resonance radiation at  $\lambda = 206.23\text{ nm}$  { $I[5p^46s(^2P_{3/2}) \leftarrow 5p^5(^2P^0_{1/2})]$ }

following their generation by pulsed irradiation. This method is considerably more sensitive and reliable than plate photometry<sup>8,9</sup> and we have compared rate data derived from this technique both with plate intensity measurements in the ultra-violet and vacuum ultra-violet<sup>8,9</sup> and with time-resolved atomic emission measurements in the infra-red<sup>10,11</sup>. Barile and Solo<sup>12</sup> have briefly described a similar method but report no detailed kinetic data. We have further shown that the sensitivity and reproducibility of this method permits its employ in the determination of rate data for the collisional quenching of  $I(5^2P_{1/2})$  over a wide range of temperature where very small energy barriers, both positive and "negative", are involved<sup>13</sup>. This previous work using attenuation of resonance radiation has been concerned with the *physical* processes of spontaneous emission<sup>8</sup>, diffusion<sup>8</sup> and spin orbit relaxation on collision<sup>8,9,13</sup>. In the present paper, we describe rate data for the *chemical* reactions of  $I(5^2P_{1/2})$  with a number of molecules.  $I(5^2P_{1/2})$  is generated by the pulsed irradiation of  $CF_3I$  and monitored photoelectrically in absorption by the attenuation procedure. The resulting data, where possible, are compared with the results of plate photometry. The present investigation also permits, in some cases, the temperature dependence of the rates of the chemical reactions of the excited atom to be studied in detail, and the results of this work are also reported.

#### EXPERIMENTAL

The experimental arrangement was similar to that described hitherto<sup>9,13</sup>.  $I(5^2P_{1/2})$  was generated by the ultra-violet flash photolysis ( $E = 500$  J) of  $CF_3I$  in the presence of excess helium buffer gas to maintain the temperature of the chosen ambient conditions ( $p_{He}:p_{CF_3I}::\sim 4000:1$ ). A double-walled quartz reaction vessel was employed to minimize photodecomposition of the gas added for reaction with the electronically excited iodine atom. Thus the annular space (thickness 1 cm) of this coaxial vessel ( $l = 30$  cm) contained the appropriate gaseous filter material for the particular reactant gas. This was generally the reactant gas itself at higher pressure. The following filters were employed (with  $p_{total\ with\ N_2} = 79.8$  kN m<sup>-2</sup>):

Reactant gas	Filter
$Cl_2$	$p_{Cl_2} = 39.9$ kN m <sup>-2</sup>
$Br_2$	$p_{Br_2} = 26.6$ kN m <sup>-2</sup>
ICl	$p_{ICl} = 4.0$ kN m <sup>-2</sup> . No significant effect was observed on the yield or kinetic decay of $I(5^2P_{1/2})$ by replacement of the filter material after each flash
IBr	$p_{IBr} = 26.6$ kN m <sup>-2</sup>
NOCl	$p_{NOCl} = 6.7$ kN m <sup>-2</sup> . The filter material was changed after each flash
NOBr	$p_{NOBr} = 6.7$ kN m <sup>-2</sup> . The filter material was changed after each flash

The photolysis lamp and the coaxial filter and vessel assembly were housed in a furnace, the kinetic measurements being carried out in the temperature range 294–421 K. Thermocouples (copper–constantan) placed at each end on the outer surface of the filter jacket indicated no significant temperature gradient across the length of the vessel.

The spectroscopic source comprised light at  $\lambda = 206.23$  nm  $\{I[5p^46s(^2P_{3/2}) \rightarrow 5p^5(^2P^0_{1/2})]\}$  from a sealed microwave-powered lamp containing iodine<sup>14</sup>, taken radially and focused through the reaction vessel onto the slit of a medium quartz spectrograph (Hilger). The concentration profiles of  $I(^2P_{1/2})$  were monitored photoelectrically by the transient variation in light absorption at  $\lambda = 206.23$  nm. The photomultiplier (E.M.I. 9783) housing was situated in the focal plane of the spectrograph and the resulting photoelectric pulses were displayed oscillographically and photographed for subsequent kinetic analysis. The overall time constant of the detection system was always less than 1.5% of the reaction time constant. Measurements were not carried out until at least 300  $\mu$ s after the initiating pulse on account of the effect of scattered light.

### Materials

Spectroscopically pure bulb krypton (British Oxygen Co. Ltd.) for the photoflash lamp was used directly. Helium buffer gas and  $CF_3I$  were employed as described hitherto<sup>13</sup>. Cylinder chlorine (Matheson Co.) was trapped at liquid nitrogen temperature ( $-196^\circ\text{C}$ ), thoroughly degassed and fractionally distilled from a  $CO_2$ /acetone slush ( $-80^\circ\text{C}$ ) to  $-196^\circ\text{C}$ . Bromine (Fisons Analytical Reagent) was thoroughly degassed and fractionally distilled from a  $CO_2/CCl_4$  slush ( $-22^\circ\text{C}$ ) to  $-196^\circ\text{C}$ .  $ICl$  (Fisons Laboratory Reagent) was thoroughly degassed and fractionally distilled from  $-22^\circ\text{C}$  to  $-196^\circ\text{C}$ .  $IBr$  (Fisons Laboratory Reagent) was degassed and sublimed several times under vacuum.  $NOCl$  and  $NOBr$  were prepared by the direct action of  $NO$  on  $Cl_2$  and  $Br_2$ , respectively. Cylinder  $NO$  (Matheson Co.) was trapped at  $-196^\circ\text{C}$ , degassed and fractionally distilled from  $-80^\circ\text{C}$  to  $-196^\circ\text{C}$ .  $Cl_2$  and  $Br_2$  were purified as given above. Nitric oxide and the appropriate halogen were mixed in the ratio of 2:1 and allowed to stand for 3 days. The product was trapped at  $-80^\circ\text{C}$  and excess nitric oxide was pumped away. For  $NOBr$ , a cold finger at  $-20^\circ\text{C}$  was maintained in the mixing bulb. The nitrosyl halide was degassed, fractionally distilled from  $-22^\circ\text{C}$  to  $-196^\circ\text{C}$  and stored in the dark.

### RESULTS AND DISCUSSION

Previous work<sup>6</sup> on single temperature kinetic measurements of  $I(^2P_{1/2})$  by plate photometry has shown that chemical reaction takes place on collision of this excited atom with the molecules  $Cl_2$ ,  $Br_2$ ,  $ICl$  and  $IBr$ . Further removal of  $I(^2P_{1/2})$  by the products of these chemical reactions, especially with  $Cl_2$  and  $Br_2$  *i.e.*  $ICl$

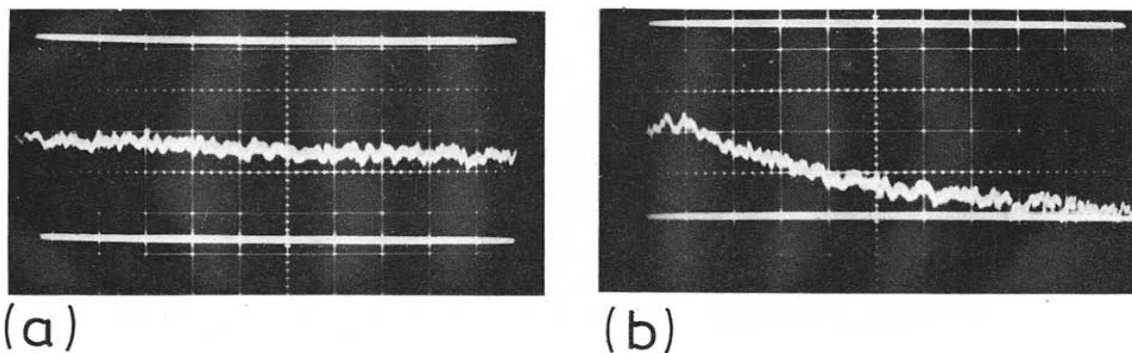


Fig. 1. Typical oscilloscopic traces indicating the decay of  $I(5^2P_{1/2})$  in the presence of chlorine obtained by monitoring the absorption of light at  $\lambda = 206.23 \text{ nm} \{I[5p^4 6s(2P_{3/2}) \leftarrow 5p^5(2P^0_{1/2})]\}$ .  $p_{CF_3I} = 0.67 \text{ N m}^{-2}$ ,  $p_{\text{total with He}} = 2.66 \text{ kN m}^{-2}$ ;  $E = 500 \text{ J}$ . Time scale =  $200 \mu\text{s}$  per division (delayed trigger  $200 \mu\text{s}$ ).  $p_{Cl_2}$  ( $\text{N m}^{-2}$ ): (a) 0.0; (b) 60.

and  $I\text{Br}$ , has hitherto<sup>6</sup> been included in the kinetic analysis. However, in the present experiments, this effect is minimized by carrying out measurements in the range where the ratio of  $[\text{Reactant}]/[I(5^2P_{1/2})]$  is optimized, namely, by employing the largest ratio compatible with the time resolution of the method. On the general basis of the kinetic data derived from plate photometry<sup>6</sup>, the conditions for eliminating significant contributions by back reactions are satisfied here for the experiments with  $\text{Cl}_2$  and  $\text{Br}_2$ , especially at the higher side of the concentration range. Plate intensity measurements have also shown that the removal of  $I(5^2P_{1/2})$  at room temperature by  $\text{NOCl}$  and  $\text{NOBr}$  is dominated by rapid halogen atom abstraction<sup>7</sup>. Thus, in this study, the collisional removal of the excited atom is ascribed to chemical reaction in all cases. Kinetic spectroscopy employing photographic measurements provides a useful basis for the photoelectric method in indicating the nature of the product distribution. However, the sensitivity of photographic detection is often inadequate for many experiments involving attenuation of atomic resonance radiation where the atomic concentrations being monitored are extremely low.

Figure 1 shows typical oscilloscopic traces indicating the decay of  $I(5^2P_{1/2})$  in the presence of chlorine. The transient absorption of light at  $\lambda = 206.23 \text{ nm}$  by  $I(5^2P_{1/2})$ , obtained by attenuation of the resonance radiation, is expressed in the form of the modified Beer–Lambert law<sup>15</sup>:

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

where the symbols have their usual significance<sup>15</sup>. We employ the value of  $\gamma = 0.71$  obtained hitherto<sup>8, 9, 13</sup> with this system for the total pressure and temperatures to be used in this investigation. Thus  $(1/\gamma) \ln[\ln(I_0/I_{\text{tr}})]$  is a logarithmic measure of the concentration of the excited atom. For the nitrogen halides, account must be taken of the change in  $I_0$  due to the absorption of light by these molecules and also by product  $\text{NO}$  at  $\lambda = 206.23 \text{ nm}$ .

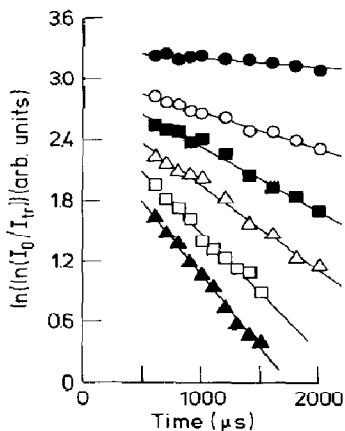


Fig. 2. Pseudo first-order plots for the decay of  $I(5^2P_{1/2})$  in the presence of different pressures of chlorine obtained by monitoring the absorption of light at  $\lambda = 206.23$  nm (296 K).  $p_{CF_3I} = 0.67$  N m $^{-2}$ ,  $p_{total}$  with He = 2.66 kN m $^{-2}$ ;  $E = 500$  J.  $p_{Cl_2}$  (N m $^{-2}$ ): ●, 0.0; ○, 8.2; ■, 17.3; △, 30.0; □, 46.2; ▲, 60.0.

Figure 2 contains first-order plots for the decay of  $I(5^2P_{1/2})$  in the presence of chlorine. The slopes of these plots ( $-\gamma k'$ ), together with the value of  $\gamma$ , yield the overall decay coefficient,  $k'$ , for a particular concentration of added reactant gas, in this case, chlorine.  $k'$  is then expressed in the form.

$$k' = K + k_R[R] \quad (\text{ii})$$

where  $k_R$  is the second order rate constant for the chemical reaction of  $I(5^2P_{1/2})$  with the reactant gas, R.  $K$  represents a first-order coefficient for the removal of the excited atom by spontaneous emission, diffusion to the walls and quenching by the parent molecule,  $CF_3I$ , and by any impurity. This is a constant for a given series of kinetic runs from which each value of  $k_R$  at a given temperature is obtained. The terms of which  $K$  is comprised have been investigated hitherto<sup>2</sup>. Two recent examples of such studies are the measurement of the coefficients for spontaneous emission and diffusion both by spontaneous emission itself in the infra-red [ $I(5^2P_{1/2}) \rightarrow I(5^2P_{3/2}) + h\nu$ , 1315 nm]<sup>16</sup> and attenuation of resonance radiation in the ultra-violet<sup>8</sup>. In the present system,  $K$  is small by comparison with the large term  $k_R[R]$  for rapid collisional removal.

The variation of the first-order coefficient for the removal of  $I(5^2P_{1/2})$  by  $Cl_2$ , derived from the slopes of the plots in Fig. 2, is presented in Fig. 3, together with similar data for various temperatures up to 421 K. The slopes of these plots (Fig. 3) yield  $k_{Cl_2}$  for the different temperatures. Figures 4 and 5 give the rate data for the reaction of the excited atom with  $Br_2$ ,  $IBr$ ,  $ICl$ ,  $NOCl$  and  $NOBr$  at room temperature in the form of eqn. (ii), together with that for  $NOCl$  at 358 K. The temperature dependence of the reaction rate constants for these gases is *very small*. Further, thermal decomposition of some of the reactant gases is expected for the higher temperatures employed. Corrections for the effects of the shift in equilibria

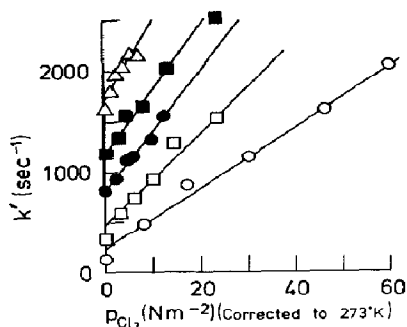


Fig. 3. Pseudo first-order rate coefficients ( $k'$ ) ( $\gamma$ -corrected) for the decay of  $I(5^2P_{3/2})$  at various temperatures in the presence of different pressures of chlorine.  $p_{CF_3I} = 0.67 \text{ N m}^{-2}$ ,  $p_{\text{total with He}} = 2.66 \text{ kN m}^{-2}$ ;  $E = 500 \text{ J}$ .  $\circ$ , ( $296 \text{ K}$ );  $\square$ ,  $k' + 200 \text{ s}^{-1}$  ( $337 \text{ K}$ );  $\bullet$ ,  $k' + 600 \text{ s}^{-1}$  ( $365 \text{ K}$ );  $\blacksquare$ ,  $k' + 1000 \text{ s}^{-1}$  ( $383 \text{ K}$ );  $\triangle$ ,  $k' + 1400 \text{ s}^{-1}$  ( $421 \text{ K}$ ).

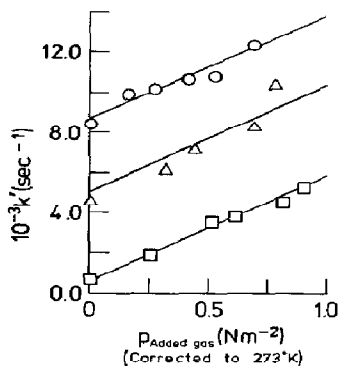


Fig. 4. Pseudo first-order rate coefficients ( $k'$ ) ( $\gamma$ -corrected) for the decay of  $I(5^2P_{3/2})$  in the presence of  $\text{Br}_2$ ,  $\text{ICl}$  and  $\text{IBr}$  at different pressures.  $p_{CF_3I} = 0.67 \text{ N m}^{-2}$ ,  $p_{\text{total with He}} = 2.66 \text{ kN m}^{-2}$ ;  $E = 500 \text{ J}$ ;  $T = 296 \text{ K}$ .  $\square$ ,  $\text{IBr}$ ;  $\triangle$ ,  $k' + 4000 \text{ s}^{-1} \text{ Br}_2$ ;  $\circ$ ,  $k' + 8000 \text{ s}^{-1} \text{ ICl}$ .

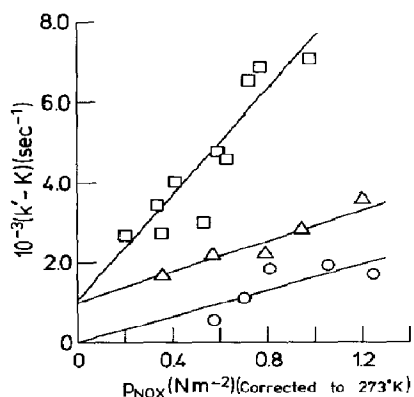


Fig. 5. Pseudo first-order rate coefficients ( $k'$ ) ( $\gamma$ -corrected, relative to that for  $p_{\text{NOX}} = 0$ ) for the decay of  $I(5^2P_{3/2})$  in the presence of  $\text{NOCl}$  and  $\text{NOBr}$ .  $p_{CF_3I} = 0.67 \text{ N m}^{-2}$ ,  $p_{\text{total with He}} = 2.66 \text{ kN m}^{-2}$ ;  $E = 500 \text{ J}$ .  $\circ$ ,  $\text{NOCl}$  ( $296 \text{ K}$ );  $\triangle$ ,  $k' + 1000 \text{ s}^{-1}$  ( $358 \text{ K}$ )  $\text{NOCl}$ ;  $\square$ ,  $k' + 2000 \text{ s}^{-1}$  ( $296 \text{ K}$ )  $\text{NOBr}$ .

TABLE 1

SECOND ORDER RATE CONSTANTS FOR THE REACTIONS OF I( $5^2P_{1/2}$ ) WITH  $Cl_2$ ,  $Br_2$ ,  $ICl$ ,  $IBr$ ,  $NOCl$  AND  $NOBr$  AT ROOM TEMPERATURE

Reactant gas	$k_R$ ( $cm^3$ molecule $^{-1}$ sec $^{-1}$ )
$Cl_2$	$1.3 \pm 0.1 \times 10^{-13}$ (296 K) $2.1 \pm 0.3 \times 10^{-13}$ (300 K) (plate photometry) <sup>6</sup>
<i>c.f.</i> I( $5^2P_{3/2}$ ) + $Cl_2 \rightarrow ICl + Cl$	$6.1 \times 10^{-21}$ (300 K) <sup>17,6</sup>
$Br_2$	$2.2 \pm 0.5 \times 10^{-11}$ (291 K) $1.5 \pm 0.2 \times 10^{-12}$ (300 K) (plate photometry) <sup>6</sup>
<i>c.f.</i> I( $5^2P_{3/2}$ ) + $Br_2 \rightarrow IBr + Br$	$\sim 2.7 \times 10^{-14}$ (300 K) <sup>6</sup>
$ICl$	$2.4 \pm 0.5 \times 10^{-11}$ (298 K) $3.4 \pm 0.2 \times 10^{-12}$ (300 K) (plate photometry) <sup>6</sup>
$IBr$	$2.0 \pm 0.1 \times 10^{-11}$ (296 K) $4.3 \pm 0.3 \times 10^{-12}$ (300 K) (plate photometry) <sup>6</sup> $\sim 10^{-17}$ (300 K) <sup>6</sup>
<i>c.f.</i> I( $5^2P_{3/2}$ ) + $IBr \rightarrow I_2 + Br$	
$NOCl$	$7.0 \pm 2.0 \times 10^{-12}$ (296 K) $6.2 \pm 0.8 \times 10^{-12}$ (300 K) (plate photometry) <sup>7</sup>
$NOBr$	$2.5 \pm 0.4 \times 10^{-11}$ (296 K) $9.6 \pm 0.8 \times 10^{-12}$ (300 K) (plate photometry) <sup>7</sup>

on the quenching of I( $5^2P_{1/2}$ ) cannot be readily made with the present measurements, particularly on account of the comparable rates for removal by the components in the equilibria (*e.g.*  $IBr$ ,  $I_2$  and  $Br_2$ <sup>7,18</sup>) and the rate dependences of the equilibrium shifts. The observed temperature dependence of  $k_R$  for  $Cl_2$  and  $Br_2$  was small and clear. The rate constants for  $ICl$  and  $IBr$  were scattered within a limited range over the temperature employed ( $k_{ICl}$ ,  $T = 296$ – $418$  K, 9 determinations;  $k_{IBr}$ ,  $T = 294$ – $408$  K, 12 determinations) and indicated no significant variation with temperature. The activation energies for reaction with these gases were set at zero and the magnitude of the scatter is reflected in the error in the mean value for the rate constants (Table 1). The values of  $k_{NOCl}$  were scattered over the same temperature range, indicating a very small activation energy. The variation of  $k_{NOBr}$  with temperature was not pursued, especially on account of thermal

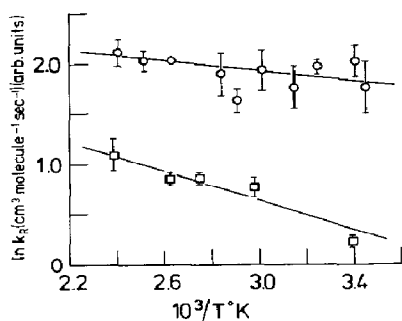


Fig. 6. Arrhenius plots of the rate constants ( $k_R$ ) for the reaction of I( $5^2P_{1/2}$ ) with  $Cl_2$  and  $Br_2$ .  $\square$ ,  $Cl_2$  ( $\ln 10^{13} + \ln k$ );  $\circ$ ,  $Br_2$  ( $1 + \ln 10^{11} + \ln k$ ).

TABLE 2

ARRHENIUS PARAMETERS FOR THE REACTIONS OF  $I(5^2P_{3/2})$  WITH VARIOUS MOLECULES

Reaction	$\log_{10} A$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ )	$E$ ( $\text{kcal mole}^{-1}$ )	$\Delta H$ ( $\text{kcal}$ ) <sup>6,7</sup>	$P = A/Z_{300K}^{\text{coll}}$
$I(5^2P_{3/2}) + \text{Cl}_2 \rightarrow \text{ICl} + \text{Cl}$ <i>c.f.</i>	$-11.6 \pm 0.2$	$1.6 \pm 0.3$	-14.3	$1.0 \times 10^{-2}$
$I(5^2P_{3/2}) + \text{Cl}_2 \rightarrow \text{ICl} + \text{Cl}^{17,6}$	-11.5	12.0	7.5	$1.0 \times 10^{-2}$
$I(5^2P_{3/2}) + \text{Br}_2 \rightarrow \text{IBr} + \text{Br}$	$-10.4 \pm 0.2$	$0.4 \pm 0.3$	-18.2	0.3
$I(5^2P_{3/2}) + \text{ICl} \rightarrow \text{I}_2 + \text{Cl}$	$-10.8 \pm 0.1$	0	-7.7	0.1
$I(5^2P_{3/2}) + \text{IBr} \rightarrow \text{I}_2 + \text{Br}$ <i>c.f.</i>	$-10.7 \pm 0.3$	0	-15.4	0.1
$I(5^2P_{3/2}) + \text{I}_2 \rightarrow \text{I}_2 + \text{I}^{13}$	$-13.4 \pm 0.7$	$-3.3 \pm 1.1$	-21.7	$2.2 \times 10^{-4}$
$I(5^2P_{3/2}) + \text{NOCl} \rightarrow \text{ICl} + \text{NO}$	$-10.6 \pm 0.2$	$0.6 \pm 0.3$	-33.8	0.2

decomposition. The Arrhenius plots [ $k = A \exp(-E/RT)$ ] for the chlorine and bromine data are given in Fig. 6 and emphasize the small variations in rate that arise in this system over a temperature range of  $\sim 120$  K.

Table 1 lists the rate constants at room temperature for the removal of  $I(5^2P_{1/2})$  by the various collision partners investigated here. The result for chlorine is in reasonable accord with that obtained from plate photometry<sup>6</sup> but the data from the present method for  $\text{Br}_2$ ,  $\text{IBr}$  and  $\text{ICl}$  indicate more rapid removal than reported hitherto<sup>6</sup>. The attenuation data are to be preferred on account of the sensitivity of the method which involves photoelectric measurements across the complete decay curve of the excited atom in a single reaction mixture and which enables these studies to be undertaken, uncomplicated by the kinetic effects of secondary reactions. Further, the data have been investigated here in greater detail over a wide temperature range. The results for  $\text{NOCl}$  and  $\text{NOBr}$  (Table 1) are again in reasonable agreement with the rate constants obtained by plate photometry<sup>7</sup>. Where possible, the results for the analogous reactions of  $I(5^2P_{3/2})$  are given for comparison (Table 1).

Table 2 lists the Arrhenius parameters obtained from the present investigation, together with those for  $I(5^2P_{3/2}) + \text{Cl}_2$  derived<sup>6</sup> from data for the reaction of  $\text{Cl} + \text{ICl}$  reported by Thrush *et al.*<sup>17</sup>, and those given previously for  $I(5^2P_{3/2}) + \text{I}_2$  employing this method<sup>13</sup>. The Arrhenius parameters for the reactions of  $I(5^2P_{1/2})$  and  $I(5^2P_{3/2})$  with  $\text{Cl}_2$  (Table 2) are particularly interesting. Firstly, the  $A$  factors for both reactions are two orders of magnitude smaller than the collision numbers: this may be expected for the excited atom where transitions from one potential energy surface to another may be involved but not for the ground state atoms. Secondly, the difference in reaction rates arises from the activation energies (Table 2) which indicate that different transition states are involved in the two cases. There appears to be a fundamental difference between the reactions of  $I(5^2P_{1/2})$  with  $\text{Cl}_2$  and  $\text{Br}_2$ , and that with  $\text{I}_2$ <sup>13</sup>. For  $\text{Cl}_2$  and  $\text{Br}_2$ , the rate constants are characterized by small positive activation energies whereas for  $I(5^2P_{1/2}) + \text{I}_2$ , a "negative



TABLE 3

SECOND ORDER RATE CONSTANTS ( $k$ , 300 K) FOR SOME REACTIONS OF THE CHLORINE ATOM IN SPECIFIC SPIN ORBIT STATES WITH ICl

Reaction	$k$ (cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup> )
Cl( $^3P_{\frac{1}{2}}$ ) + ICl $\rightarrow$ I( $5^2P_{\frac{1}{2}}$ ) + Cl <sub>2</sub> (-1)	$1.0 \times 10^{-22}$
Cl( $^3P_{\frac{1}{2}}$ ) + ICl $\rightarrow$ I( $5^2P_{\frac{3}{2}}$ ) + Cl <sub>2</sub> (2)	$\sim 3 \times 10^{-11}$ (19)
Cl( $^3P_{\frac{3}{2}}$ ) + ICl $\rightarrow$ I( $5^2P_{\frac{3}{2}}$ ) + Cl <sub>2</sub> (3)	$4.6 \times 10^{-16}$ (17)

activation energy" of  $-3.3$  kcal is clearly established<sup>13</sup>. Further, the Arrhenius  $A$  factor for removal with I<sub>2</sub> is smaller by some two orders of magnitude. It is thus tempting to speculate, contrary to an earlier suggestion<sup>2</sup>, that, by contrast with Cl<sub>2</sub> and Br<sub>2</sub>, I( $5^2P_{1/2}$ ) undergoes physical relaxation on collision with molecular iodine and that an abstraction reaction does not occur. On the other hand, the negative activation energy may indicate the role of an I<sub>3</sub> complex where the identity of the original excited atom is lost. An isotopic labelling experiment is required to differentiate between chemical reaction and physical relaxation arising from the collision of I( $5^2P_{1/2}$ ) and I<sub>2</sub>.

For an approximate comparison of some rate constants of the chlorine atom in defined spin orbit states with the ICl molecule, we employ the crude assumption that the measured rate of the *chemical reaction*<sup>6</sup> between I( $5^2P_{1/2}$ ) + Cl<sub>2</sub> (Tables 1 and 2) corresponds to a process yielding *specifically* Cl( $3^2P_{1/2}$ ):



If we further assume that the  $^2P_{1/2}$  states of the chlorine and iodine atoms are not in equilibrium with the  $^2P_{3/2}$  ground states and that the excited states may be treated as separate, metastable species, we may invoke the principle of detailed balancing and calculate an effective equilibrium constant of  $K_1 = 1.3 \times 10^9$  by statistical mechanics using the spectroscopic data given by Herzberg<sup>18</sup>. Hence, we derive from the measured value of  $k_1$  (Table 1), an approximate value for  $k_{-1}$  (300 K). This is given in Table 3 with other kinetic data reported hitherto<sup>17,19</sup>. The resulting Arrhenius  $A$  factor for reaction (-1) may be calculated from  $k_1$  (Table 2) and  $K_1$ , yielding  $k_{-1} = 4.2 \times 10^{-13} \exp(-13.3 \text{ kcal}/RT)$  cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup>.

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