Recombination of iodine atoms in dilute solutions of argon†

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The reaction \(2I + \text{Ar} \rightarrow I_2 + \text{Ar}\) was studied at 298, 323 and 423 K by flash photolysis. The overall rate constant, \(k_{\text{obs}}\), for this reaction is a linear function of \([I_2]/[\text{Ar}]\), but below \([I_2]/[\text{Ar}] \sim 10^{-4}\), the relation becomes non-linear and \(k_{\text{obs}}\) falls below extrapolated values. The fall-off is explained in terms of a mechanism involving an IAr intermediate:

\[
\begin{align*}
I + \text{Ar} &\rightarrow \text{IAr} \\
\text{IAr} + I &\rightarrow I_2 + \text{Ar}.
\end{align*}
\]

The equilibrium separation in such an IAr complex is 0.55 nm and the binding energy is 6.3 kJ mol\(^{-1}\) (1.5 kcal mol\(^{-1}\)). This mechanism predicts the onset of the fall-off in agreement with the available experimental data. Moreover, the temperature dependence of this onset and the temperature dependence of the recombination rate constant from 298 to 1500 K are also satisfactorily explained.

In addition to the above, the new mechanism yields quantitative agreement between our new rate constants and those reported previously. These combined data for 298 K yield a value of \(3.00 \pm 0.16 \times 10^9\) \(\text{I}_2\) mol\(^{-2}\) s\(^{-1}\) for the rate constant for the reaction

\(2I + \text{Ar} \rightarrow I_2 + \text{Ar}\),

and one of \(1.00 \pm 0.09 \times 10^{12}\) \(\text{I}_2\) mol\(^{-2}\) s\(^{-1}\) for \(2I + I_2 \rightarrow 2I_2\).

Several other mechanisms are also considered, including some previously suggested in the literature. It is shown that none of these explains satisfactorily all the experimental data. However, most of the available experimental data could be explained, if it were assumed that the recombination proceeds via an unobserved electronically excited \(I_2^*\) formed from two \(\text{I}^2\text{P}_1\) atoms, with a potential well 21 to 29 kJ mol\(^{-1}\) deep (5 to 7 kcal mol\(^{-1}\)).

Introduction

The termolecular recombination of iodine atoms in the presence of a third body, \(M\):

\[
2I + M \rightarrow I_2 + M,
\]

was studied by Rabinowitch & Wood (1936), using a photostationary method, and by Christie, Harrison, Norrish & Porter (1955), Strong, Chien, Graf & Willard

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(1957), Bunker & Davidson (1958), Engleman & Davidson (1960), Kramer, Hanes & Bair (1961) and Porter & Smith (1961), all of whom used flash photolysis. Rabinowitch (1937) suggested that such recombination proceeds via an I–M complex. If more than one third body (M_i) contributes to the reaction, Rabinowitch’s mechanism may be generalized as follows:

\[ I + M_i \xrightarrow{k_{4i}} IM_i, \]  
\[ IM_i + I \xrightarrow{k_{4i}} I_2 + M_i, \]  
\[ IM_i + IM_j \xrightarrow{k_{5ij}} I_2 + M_i + M_j, \]

\[ \frac{d[I_2]}{dt} = \sum_{i=1}^{N} k_{4i} [I] [IM_i] + \sum_{i=j}^{N} \sum_{j=1}^{N} k_{5ij} [IM_i] [IM_j]. \]  

Assuming that equilibria (3) are maintained, equation (6) reduces to

\[ \frac{d[I_2]}{dt} = \sum_{i=1}^{N} k_{4i} K_{3i}[I]^2 [M_i] + \sum_{i=j}^{N} \sum_{j=1}^{N} k_{5ij} K_{3i} K_{3j}[I]^2 [M_i] [M_j], \]  

where \( K_{3i} = k_{4i}/k_{-4i} \) is the equilibrium constant for reaction (3).

The experimental rate constant \( k_{\text{obs}} \) (equation (2)) has usually been obtained by optically monitoring the concentration of I_2 following the flash. In this case, the apparent iodine atom concentration is

\[ [I_{\text{app}}] = [I] + \sum_{i=1}^{N} [IM_i] = [I] \left( 1 + \sum_{i=1}^{N} K_{3i}[M_i] \right), \]  

where \([I_{\text{app}}]\) is twice the concentration of dissociated molecular iodine (i.e.

\[ \frac{d[I_2]}{dt} = -\frac{1}{2} \frac{d[I_{\text{app}}]}{dt}. \]  

Replacing \([I]\) in equation (2) by \([I_{\text{app}}]\), and combining the result with equation (7), one obtains

\[ k_{\text{obs}} = \frac{(d[I_2]/dt)[I_{\text{app}}]^{-2}[M_1]^{-1}}{\left( 1 + \sum_{i=1}^{N} K_{3i}[M_i] \right)^{-2} \left( k_{4,1} K_{3,1} + \sum_{i=2}^{N} k_{4i} K_{3i}[M_i]/[M_1] \right. \right. \]
\[ \left. \left. + \sum_{i=j}^{N} \sum_{j=1}^{N} K_{3j} k_{5ij} K_{3j}[M_i]/[M_j]/[M_1] \right) \right), \]  

where \( M_1 \) is the diluent gas which is present in large excess.

In the past, it has usually been implicitly assumed that concentrations of IM_i complexes are negligible compared with the iodine atom concentration, and that \( K_{3i}[M_i] \ll 1 \) for all \( i \). The contribution of (5) also was usually neglected. In this case, since in most experiments the only third bodies available were molecular iodine and a single diluent gas, equation (9) reduces to

\[ k_{\text{obs}} = k_{4M} K_{3M} + k_{4I_2} K_{3I_2} [I_2]/[M], \]

\[ = k_M + k_{I_2}[I_2]/[M]. \]
Equation (10) has been verified for various M over an appreciable range of \([I_2]/[M]\) ratios (Christie et al. 1955). However, Christie et al. (1955) and Kramer et al. (1961) observed that if the \([I_2]/[M]\) ratio is less than about \(2 \times 10^{-4}\), \(k_{\text{obs}}\) falls below the extrapolation of results obtained at higher concentration ratios. Moreover, Christie (1962) deduced the existence of the fall-off from the results of Bunker & Davidson (1958). Since fall-off occurs at low dilution ratios, it cannot be ascribed to the thermal effects described by Burns & Hornig (1960) and by Burns (1967). Christie et al. (1955) suggested that the fall-off could be attributed to the formation of metastable iodine molecules which are deactivated only by collisions with \(I_2(3^3\Sigma^+_g)\). However, they made no attempt to identify the metastable iodine.

The present work was undertaken to investigate this low concentration ratio fall-off and to determine the nature of the intermediate that would account for its existence.

**Experimental**

The iodine recombination reaction in argon was investigated in two conventional flash photolysis apparatuses. The reaction vessel of apparatus I was double walled, constructed of quartz tubing, 167 cm long, and had a 35 mm diameter. The flash lamp, also made of quartz tubing, was 175 cm long and had a 9 mm diameter. The flash was generated by discharging through the lamp a 10 \(\mu\)F capacitor, at typically 15 kV. The lamp and the reaction vessel were mounted parallel within a polished aluminium reflector. The reflector was wrapped in heating tape and asbestos insulation. The reaction vessel could be heated to 450 K; the temperature fluctuation along the length of the cell was less than 2 K. A greaseless vacuum system was constructed for these experiments; Teflon type stopcocks were used in the vacuum system.

Flash photolysis apparatus II was similar, though physically smaller. A single walled reaction vessel and flash lamp were mounted in a furnace; the portions of the vacuum system containing iodine were enclosed in an oven which could be heated to 1200 K. Greaseless stopcocks were used in these portions of the vacuum system.

The recombination was monitored using a quartz incandescent lamp, collimating lenses and an RCA 931-A-photomultiplier tube. The analyzing beam was rendered monochromatic using an interference filter and a Corning no. 3387 cut-off filter. This combination of filters had a transmission peak at 487 nm with a peak half-width of 7 nm. The amplified output of the photomultiplier was displayed on an oscilloscope and photographed. Four to seven photographs were taken and combined to obtain one value of the rate constant. A second photomultiplier monitored the drift in intensity of the analysing light. The response time of the photomultiplier circuits was better than 1.5 \(\mu\)s.

The iodine molecule concentration was determined from the optical transmission of the cell before and after filling with an \(I_2\)-Ar gas mixture; for this purpose, the decadic extinction coefficient was determined for each apparatus. In these determinations, an ice bath was used to produce a standard iodine vapour pressure. The vapour pressure–temperature relation of Gillespie & Fraser (1936) was used.
RESULTS

To obtain $k_{\text{obs}}$, the data were reduced according to the integrated form of equation (2). For ratios $[I_2]/[\text{Ar}] > 10^{-4}$ ('high ratio' results), the values of $k_{\text{obs}}$ (shown in

![Figure 1. Recombination rate constants, $k_{\text{obs}}$, against $[I_2]/[\text{Ar}]$ at room temperature: BD, Bunker & Davidson (1958); CHNP, Christie et al. (1955); O, Strong et al. (1957); ●, Kramer et al. (1961); ..., this work-apparatus 1; x, this work-apparatus 2.]

![Figure 2. Recombination rate constants, $k_{\text{obs}}$, against $[I_2]/[\text{Ar}]$ at 323 K (▲) and 423 K (●), obtained from apparatus I.]

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figures 1 and 2) were a linear function of $[I_2]/[Ar]$, as predicted by equation (10). The values of $k_{Ar}$ and $k_{I_2}$ defined as the intercept and slope of this linear plot, agree well with those in the literature (see table 1) except that the present values of $k_{Ar}$ at 298 and 323 K are somewhat lower than those of previous investigators. However, this discrepancy may be partially explained in terms of the mechanism which accounts for the low concentration ratio fall-off. This mechanism will be described later in this paper.

**Table 1. Summary of results on recombination of iodine atoms in Ar and I$_2$, interpreted according to equation (10)**

<table>
<thead>
<tr>
<th>T/K</th>
<th>$10^{-9} k_{Ar}/I_2$ mol$^{-2}$ s$^{-1}$</th>
<th>$10^{-12} k_{I_2}/I_2$ mol$^{-2}$ s$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>3.3 ± 0.36</td>
<td>0.85</td>
<td>Christie et al. (1955)</td>
</tr>
<tr>
<td></td>
<td>2.9 ± 0.3</td>
<td>1.9 ± 0.2</td>
<td>Bunker &amp; Davidson (1958)</td>
</tr>
<tr>
<td></td>
<td>2.4 ± 0.1</td>
<td>1.4 ± 0.2</td>
<td>This work, apparatus II</td>
</tr>
<tr>
<td>323</td>
<td>3.15</td>
<td>0.973 ± 0.1‡</td>
<td>Engleman &amp; Davidson (1960)</td>
</tr>
<tr>
<td></td>
<td>2.99 ± 0.15†</td>
<td>1.07 ± 0.18†</td>
<td>Engleman &amp; Davidson (1960)</td>
</tr>
<tr>
<td></td>
<td>1.9 ± 0.1</td>
<td>1.0 ± 0.1</td>
<td>This work, apparatus I</td>
</tr>
<tr>
<td>423</td>
<td>1.84</td>
<td>0.227 ± 0.053‡</td>
<td>Engleman &amp; Davidson (1960)</td>
</tr>
<tr>
<td></td>
<td>1.66 ± 0.05†</td>
<td>0.143 ± 0.038†</td>
<td>Engleman &amp; Davidson (1960)</td>
</tr>
<tr>
<td></td>
<td>1.6 ± 0.1</td>
<td>0.38 ± 0.2</td>
<td>This work, apparatus I</td>
</tr>
</tbody>
</table>

† Calculated from data obtained by Bunker & Davidson (1958).
‡ Obtained from measurements in excess of He.

**Table 2. k$_{obs}$, [I$_2$] and [Ar] room temperature, apparatus I**

<table>
<thead>
<tr>
<th>T/K</th>
<th>$10^9 k_{obs}/I_2$ mol$^{-2}$ s$^{-1}$</th>
<th>$10^5 [I_2]$ mol$^{-1}$</th>
<th>$10^2 [Ar]$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>no filter used</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.70</td>
<td>0.067</td>
<td>8.01</td>
<td></td>
</tr>
<tr>
<td>1.62</td>
<td>0.077</td>
<td>7.79</td>
<td></td>
</tr>
<tr>
<td>1.67</td>
<td>0.096</td>
<td>7.97</td>
<td></td>
</tr>
<tr>
<td>1.48</td>
<td>0.150</td>
<td>6.49</td>
<td></td>
</tr>
<tr>
<td>1.77</td>
<td>0.139</td>
<td>5.83</td>
<td></td>
</tr>
<tr>
<td>1.77</td>
<td>0.169</td>
<td>6.11</td>
<td></td>
</tr>
<tr>
<td>1.84</td>
<td>0.134</td>
<td>4.23</td>
<td></td>
</tr>
<tr>
<td>2.08</td>
<td>0.155</td>
<td>4.25</td>
<td></td>
</tr>
<tr>
<td>2.13</td>
<td>0.219</td>
<td>4.21</td>
<td></td>
</tr>
<tr>
<td>2.32</td>
<td>0.228</td>
<td>3.58</td>
<td></td>
</tr>
<tr>
<td>2.39</td>
<td>0.254</td>
<td>2.40</td>
<td></td>
</tr>
<tr>
<td>2.44</td>
<td>0.373</td>
<td>1.67</td>
<td></td>
</tr>
</tbody>
</table>

K$_2$Cr$_2$O$_7$ filter solution used

<table>
<thead>
<tr>
<th>T/K</th>
<th>$10^9 k_{obs}/I_2$ mol$^{-2}$ s$^{-1}$</th>
<th>$10^5 [I_2]$ mol$^{-1}$</th>
<th>$10^2 [Ar]$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.78</td>
<td>0.075</td>
<td>7.77</td>
<td></td>
</tr>
<tr>
<td>1.69</td>
<td>0.083</td>
<td>7.89</td>
<td></td>
</tr>
<tr>
<td>2.00</td>
<td>0.148</td>
<td>7.91</td>
<td></td>
</tr>
<tr>
<td>2.05</td>
<td>0.199</td>
<td>7.86</td>
<td></td>
</tr>
<tr>
<td>1.87</td>
<td>0.181</td>
<td>7.15</td>
<td></td>
</tr>
<tr>
<td>2.11</td>
<td>0.158</td>
<td>7.89</td>
<td></td>
</tr>
<tr>
<td>2.27</td>
<td>0.214</td>
<td>5.41</td>
<td></td>
</tr>
<tr>
<td>1.96</td>
<td>0.332</td>
<td>7.87</td>
<td></td>
</tr>
<tr>
<td>2.13</td>
<td>0.369</td>
<td>5.68</td>
<td></td>
</tr>
<tr>
<td>2.27</td>
<td>0.284</td>
<td>3.95</td>
<td></td>
</tr>
<tr>
<td>2.13</td>
<td>0.390</td>
<td>4.12</td>
<td></td>
</tr>
<tr>
<td>2.49</td>
<td>0.823</td>
<td>3.94</td>
<td></td>
</tr>
</tbody>
</table>
Room temperature rate constants for \([I_2]/[\text{Ar}] < 10^{-4}\) ('low ratio' results) fall below the linear extrapolation from those at higher ratios, in agreement with the findings of previous investigators (table 2 and figures 1 and 2).

**Discussion**

The rate constant drop-off at low concentration ratios (figures 1 and 2) may be explained in terms of the participation of an intermediate species in the reaction process. In this section several possible intermediates are considered; however, it is shown that only one of these can successfully account for all of the experimental observations.

*Participation of \(I_2(B^{3}\Pi_{0u})\)*

It was pointed out by Nikitin (1966) that the low \([I_2]/[\text{Ar}]\) fall-off may be due to the participation of electronically excited iodine molecules. Such molecules may be formed either from ground state atoms \((^2P_{\frac{1}{2}})\) or from excited iodine atoms \((^2P_{\frac{3}{2}})\). The recombination of excited atoms with ground state atoms into attractive states, one of which \((B^{3}\Pi_{0u})\) is known, may take place. It has been argued by Snider (1966) that these \(B^{3}\Pi_{0u}\) molecules deactivate to the ground state only upon collision with other \(I_2\). Thus, at low \([I_2]/[\text{Ar}]\), this route for recombination would be ineffective and the fall-off would occur. Snider also pointed out that this mechanism is not in disagreement with the data of Christie *et al.* (1955). However, Steinfeld & Klemperer (1965) found that \(B^{3}\Pi_{0u}\) molecules predissociate very readily on collision with inert gases. Therefore deactivation via collision with \(I_2\) could not be important. Moreover, the radiative lifetime of \(B^{3}\Pi_{0u}\) state is of the order of a microsecond, which is three orders of magnitude shorter than the typical recombination time. For these reasons, \(B^{3}\Pi_{0u}\) state cannot account for the observed fall-off.

*Participation of excited \(^2P_{\frac{1}{2}}\) atoms*

Another possible explanation of the fall-off involves direct participation of \(^2P_{\frac{1}{2}}\) atoms:

\[
I(^2P_{\frac{1}{2}}) + I_2 \rightarrow I(^2P_{\frac{3}{2}}) + I_2. \tag{11}
\]

Alternatively, \(^2P_{\frac{3}{2}}\) atoms may participate in the overall recombination reaction via electronically excited \(I_2\), other than \(^3\Pi_{0u}\),

\[
I(^2P_{\frac{3}{2}}) + I_2(^1\Sigma^+_g) \rightarrow I_2(\text{elec. excited}) + I(^2P_{\frac{1}{2}}) \rightarrow I_2(^1\Sigma^+_g) + I(^2P_{\frac{3}{2}}) \tag{12}
\]

in a reaction which precedes the recombination. The fall-off would then be observed at low \([I_2]/[\text{Ar}]\). Experiments suitable for testing the validity of this mechanism were carried out by Christie *et al.* (1955), who flash photolysed \(I_2\) in Ar, using a potassium dichromate filter solution in a double walled photolysis reaction vessel. This filter limited the wavelength of the photolysing light reaching the reaction mixture, so that the \(B^{3}\Pi_{0u}\) iodine molecules, formed in the photolysis were at least 800 cm\(^{-1}\) below the dissociation limit of the state. In this case the \(B^{3}\Pi_{0u}\) molecules predissociate to give two \(^2P_{\frac{3}{2}}\) atoms, thus effectively preventing the production of \(I(^2P_{\frac{1}{2}})\).
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Christie et al. (1955) found that the use of the potassium dichromate filter solution did not affect the magnitude of the rate constants. Unfortunately, only one experiment was performed in the fall-off region; it suggested that a mechanism involving reactions (11) and (12) cannot account for the abnormally small rate constants at low \([I_2]/[Ar]\). We extended the range of the Christie et al. (1955) experiments and obtained twenty-one rate constant measurements in the ‘low-ratio’ region. In eleven of these, a potassium dichromate filter solution was used; in the remainder, no filter was used. The results (table 2) indicate that the rate constants in the fall-off region may be lower by about 10% if a filter solution is not used. However, such a discrepancy is almost within experimental error. Therefore, it is concluded that while reactions (11) and (12) may contribute they are not the main cause of the observed fall-off. This conclusion is in agreement with direct measurements of the \(I(\text{2P}_3/2)\) relaxation rate due to \(I(\text{2P}_3/2) - I_2\) collisions, reported by Donovan & Husain (1965).

Participation of vibrationally excited \(I_2(X^1\Sigma_g^+)\)

To explain the fall-off at low \([I_2]/[M]\), Christie (1962) proposed the following mechanism:

\[
I + I + M \rightarrow I^*_2 + M, \quad (13)
\]

\[
I^*_2 + I_2 \rightarrow 2I_2, \quad (14)
\]

where \(I^*_2\) is a vibrationally excited ground state \((^1\Sigma_g^+)\) iodine molecule. According to this mechanism, the relaxation (14) becomes the rate determining step at low \([I_2]/[M]\) ratios. However, Shields (1960) showed that vibrational relaxation of \(I_2(\text{2P}_3/2)\) is much too fast to cause the fall-off in \(k_{\text{obs}}\) at concentration ratios of the order of \(10^{-4}\). The theoretical analyses of Nikitin (1962) and Snider (1966) also preclude an explanation involving reactions (13) and (14), which will not be further discussed here.

Participation of electronically excited \(I_2\) produced from two \(\text{2P}_3\) atoms

An alternative explanation of the fall-off involves the participation of electronically excited molecules, \(I^*_2\), produced from atoms in the ground electronic state (i.e. two \(I(\text{2P}_3)\) atoms). For the experimental situation where only \(I_2\) and a single inert gas \(M\) are present as third bodies, this mechanism may be written as

\[
I + I + M \xrightarrow{k_{11}} I_2 + M, \quad (15)
\]

\[
I + I + I_2 \xrightarrow{k_{12}} I_2 + I_2, \quad (16)
\]

\[
I + I + M \xrightarrow{k_{17}} I^*_2 + M, \quad (17)
\]

\[
I + I + I_2 \xrightarrow{k_{19}} I^*_2 + I_2, \quad (18)
\]

\[
I^*_2 + I_2 \xrightarrow{k_{20}} 2I_2, \quad (19)
\]

If more than one excited state is involved, reactions (17), (18) and (19) are repeated for each state. This mechanism is particularly interesting because it would imply
that in the fall-off region the internal (electronic) distribution function of $I_2$ differs, during recombination, from the equilibrium distribution function (Nikitin 1966).

Assuming a steady state in $I_2^e$ and the approximations inherent in equation (10), the following expression for $k_{obs}$ is obtained:

$$k_{obs} = k_{15} + (k_{16} + Kk_{19}) [I_2]/[M] - \frac{(Kk_{19} [I_2]/[M])^2}{k_{17} + (k_{18} + Kk_{19}) [I_2]/[M]}$$

$$= k_{15} + k_{16}[I_2]/[M] + \frac{Kk_{19} (k_{17} + k_{18}[I_2]/[M]) ([I_2]/[M])}{k_{17} + (k_{18} + Kk_{19}) [I_2]/[M]},$$

(20)

where

$$K = k_{17}/k_{-17} = k_{18}/k_{-18}.$$  

(21)

The mechanism (15) to (19) explains the fall-off at low $[I_2]/[M]$ provided that $k_{16}$ and $k_{18}$ are very much smaller than $Kk_{19}$. Then for the special case of very small values of $[I_2]/[M]$

$$k_{obs} \approx k_{15} + Kk_{19}[I_2]/[M],$$

(22)

and for large $[I_2]/[M]$ such that $Kk_{19} [I_2]/[M] \gg k_{17}$,

$$k_{obs} \approx k_{15} + k_{17} + (k_{16} + k_{18}) [I_2]/[M].$$

(23)

Values of the four independent parameters $k_{15}$, $k_{16} + k_{15}$, $k_{17}$ and $Kk_{19}$ were derived for the best fit of equation (20) at room temperature, for the special case $M = Ar$, using the data of Christie et al. (1955). These data were used rather than our own (table 1), because while the latter are more abundant at very small $[I_2]/[Ar]$ values, the former extend to much higher concentration ratios, and hence reach both high and low asymptotic regions. If the mechanism (15) to (19) is valid, the constants obtained should apply equally well to both sets of data.

It was found that the experimental differences between our work and those of Christie et al. are appreciable at higher $[I_2]/[Ar]$ (figure 1). On the other hand, the $Kk_{19}$ value obtained from our data (table 1) agrees well with that obtained from the Christie et al. data. This value of $Kk_{19}$, $1.6 (\pm 0.7) \times 10^{13} 12$ mol$^{-2}$ s$^{-1}$, quantitatively relates the nature of the $I_2^e$ internuclear potential which determines $K$, to the effective collision diameter buried in $k_{19}$.

The $I_2^e$ mechanism may now be tested by considering its predictions with respect to four factors. These are: (1) the nature of the internuclear potential for the $I$ complex, (2) the dependence of the ratio at which fall-off begins, ($[I_2]/[M])_{dev}$, on the nature of the third body $M$, (3) the temperature dependence of ($[I_2]/[M])_{dev}$, and (4) the apparent inconsistencies (shown in figure 1) between the experimental results obtained in different laboratories.

Chang (1967) has used perturbation theory to calculate moderately long-range interaction energies for pairs of degenerate atoms for non-resonant cases. His results show that of the sixteen molecular states formed from pairs of ground $^2P_{3/2}$ iodine atoms, at least seven other than the ground $X^3\Sigma^+_g$ state are attractive.
These are the single degenerate $^3\Pi_{\text{g}}$ state, and the doubly $\Omega$-degenerate $^3\Pi_{1u},^3\Pi_{1g}$ and $^3\Pi_{2u}$ states. Of these, only the first two are optically accessible from the ground state and only the $^3\Pi_{1u}$ has been observed (Brown 1931).

Calculations were carried out to determine the parameters of the $I^g_2$ internuclear potential which would account for the fall-off, while giving a reasonable collision diameter for reaction (19). The equilibrium constant was evaluated for a number of well depths ($E$) and equilibrium separations ($R_{\text{eq}}$) for $I^g_2$, using the expression Kim (1967)† obtained from Hill's (1955) partition function integrals:

$$K = \frac{64}{45} \frac{R_{\text{eq}}^6}{\pi^3 E^{3/2}} \frac{g_{\text{M}}}{g_{\text{A}}^2} E \frac{F(E/kT)}{kT},$$

(24)

where $g_{\text{M}}/g_{\text{A}}^2$, the ratio of molecular to atomic degeneracies, is taken to be 2/16, and $F(E/kT)$ is the generalized hypergeometric series (Erdelyi 1953):

$$\text{}_{2}F_{2}(1,1; 7/4, 9/4; E/kT).$$

(25)

Expression (24) assumes a Lennard-Jones (12-6) interaction potential for $I^g_2$.

The calculated equilibrium constants were combined with the derived value of $Kk_{19}$ to give corresponding values for $k_{19}$. From each value of $k_{19}$, the hard sphere collision diameter $\sigma_c$ for reaction (19) was calculated assuming zero activation energy and unit probability factor. In figure 3, $\sigma_c R_{\text{eq}}^6$ is plotted against $E$, showing the possible combinations of collision diameter, equilibrium separation and well depth.

† Modified for homonuclear molecules by multiplication by a statistical factor of $\frac{1}{2}$.
for \( \text{I}_2^* \). It follows from this plot that for a reasonable value of \( \sigma_c \), the value of \( E \) should be somewhere between 21 and 29 kJ mol\(^{-1}\) (5 and 7 kcal mol\(^{-1}\)). This is three times the 7.5 kJ mol\(^{-1}\) (1.8 kcal) depth of the potential well of \( \text{A}^3\Pi_{1u} \), the only observed (Brown 1931) excited \( \text{I}_2^* \) state which dissociates to two \( ^2\text{P}_3 \) atoms. However, Chang’s (1967) calculations show that at long range the \( ^3\Pi_{1g} \) and \( ^3\Pi_{2u} \) states are respectively 2 and 3\( \frac{1}{2} \) times more strongly attractive than \( \text{A}^3\Pi_{1u} \). Hence, one of these states will probably have the 21 to 29 kJ mol\(^{-1}\) well depth required of an acceptable \( \text{I}_2^* \) complex. We therefore conclude that this mechanism (equations (15) to (19)) makes an acceptable prediction for the nature of the internuclear potential of \( \text{I}_2^* \).

As a check on equation (24), the equilibrium constant \( K \) for formation of \( \text{I}_2^* \) in the \( \text{A}^3\Pi_{1u} \) state was calculated directly. The internal partition function was based on vibrational energies observed by Brown (1931) and rotational constants calculated from formulae given by Herzberg (1950). This yielded \( K = 0.0851 \text{ mol}^{-1} \), only 20\% larger than the corresponding 0.0721 mol\(^{-1}\) value generated from expression (24). This concurs with the conclusion that the 7.5 kJ (1.8 kcal) mol\(^{-1}\) deep \( \text{A}^3\Pi_{1u} \) state cannot be the main cause of the drop off.

Condition (2) can now be further tested by considering the asymptotic forms of expression (20) for very large and very small concentration ratios. An approximate value of \( ([\text{I}_2]/[\text{M}])_{\text{dev}} \) may be obtained by solving equations (22) and (23) for their point of intersection

\[
\frac{([\text{I}_2]/[\text{M}])_{\text{dev}}}{Kk_{19}} \approx k_{17}.
\]

Since the relative efficiencies of various third bodies depend principally on the stability of the intermediate \( \text{IM} \) complex, it seems reasonable to assume that the relative efficiencies are independent of the final iodine electronic state formed. Thus \( k_{15} \) and \( k_{17} \) would show the same dependence on the choice of third body \( \text{M} \), and hence \( k_{17} \propto k_{M} \), where \( k_{M} \) is the experimentally obtained intercept of equation (23). Therefore, (26) becomes

\[
([\text{I}_2]/[\text{M}])_{\text{dev}} \propto k_{M}.
\]

Christie (1962) has noted just such a linear relation between the experimental values of \( ([\text{I}_2]/[\text{M}])_{\text{dev}} \) and \( k_{M} \). Moreover, the linear relation (27) predicts that the fall-off should be observed with helium as third body at values of \( [\text{I}_2]/[\text{He}] \) which are smaller than those used by Christie et al. (1955). Thus, from this viewpoint, the data of Christie et al. supports this mechanism (equations (15) to (19)). However, the mechanism fails to explain the difference between the 298°K value of \( ([\text{I}_2]/[\text{Ar}])_{\text{dev}} \) obtained by Christie et al. (1955), i.e. \( 4 \times 10^{-4} \), and that reported here, i.e. \( 1 \times 10^{-4} \) (see figure 1).

The temperature dependence of \( ([\text{I}_2]/[\text{M}])_{\text{dev}} \) may be determined by rearrangement of equation (26) to yield

\[
([\text{I}_2]/[\text{M}])_{\text{dev}} \approx \frac{k_{-17}}{k_{19}}.
\]

Assuming that \( k_{19} \) has zero activation energy and that \( k_{-17} \) has an activation energy equal to the well depth of the internuclear interaction in \( \text{I}_2^* \) (i.e. 21 to 29 kJ mol\(^{-1}\)),
Recombination of iodine atoms in dilute solutions in argon

Equation (28) predicts a twofold increase in \((\frac{[I_2]}{[M]})_{dev}\) as temperature is increased from 298 to 323 K, and a 10 to 20-fold increase in \((\frac{[I_2]}{[M]})_{dev}\) as temperature is increased from 298 to 423 K. Although the data of this work at 323 and 423 K are somewhat scattered, it appears that this prediction is not fulfilled; the onset of the fall-off appears to be roughly independent of \(T\) (figures 1 and 2).

The fourth requirement of the mechanism, that it explain the discrepancies which figure 1 shows to exist among the results obtained in different laboratories, is also not fulfilled. This mechanism does not suggest any route by which the diverse sets of data can be made self-consistent.

The mechanism involving electronically excited \(I_2^*\) can explain the fall-off only if it is assumed that \(I_2^*\) is deactivated very efficiently by \(I_2(1\Sigma^+_g^+)\), so that the deactivation by inert gas is a slower process by a factor of \(10^{-5}\). Theoretical studies by Nikitin (1966) support such an assumption. However, Steinfeld & Klemperer (1965) found that \(I_2(1\Sigma^+_g^+)\) was only ca. seven times more efficient than \(Ar\) in the electronic de-excitation of \(I_2(3^2P_0^+)\).

Participation of intermediate IM complex

An alternative explanation for the low-ratio fall-off has been proposed by Troe & Wagner (1967), who measured the dissociation rate constant for iodine in argon in high pressure (ca. \(10\text{MNm}^{-2}; 100\text{atm}\)) shock waves. They observed a transition in the dissociation rate constant from bimolecular to unimolecular with increasing argon pressure. They suggest that the recombination rate constant should undergo a similar transition from third to second order, and by extrapolating their results to room temperature they predict that the transition argon concentration would be approximately \(70\text{mmol} \text{l}^{-1}\). A similar effect has been observed by Porter, Szabo & Townsend (1962) for iodine atom recombination in high pressures of nitric oxide chaperon.

In this case, the mechanism is that given by equations (3) to (5), where \(I_2\) and a single inert gas \(M\) are the only chaperons present for the cases experimentally considered. Furthermore, since the absolute concentrations of \(I_2\) used experimentally are always quite small, it is safe to assume that \(K_{31}[I_2] \ll 1\). In this case, (9) becomes

\[
k_{\text{obs}} = \frac{K_{3M}k_{4M} + K_{31}k_{41}[I_2]/[M] + K_{3M}^2k_{5M-M}[M]}{(1 + K_{3M}[M])^2}.
\]

The room temperature data of this work (both apparatuses) and the data of Christie et al. (1955) and of Strong et al. (1957) for \(M = Ar\) were fitted to (29) using a Hooke & Jeeves (1961) pattern search method. The best fit was obtained with a negative value of \(K_{3M}^2k_{5M-M}\), indicating that the effect of reaction (5) was less than the experimental scatter in the data.\footnote{The data were then fitted to an expression which neglected reaction (5):}

\[
k_{\text{obs}} = \frac{K_{3M}k_{4M} + K_{31}k_{41}[I_2]/[M]}{(1 + K_{3M}[M])^2}.
\]

Furthermore, a fit with the four parameters constrained to be positive yielded an insignificantly small value of \(K_{3M}^2k_{5M-M}\) which had a very large uncertainty.
TABLE 3. RATE AND EQUILIBRIUM CONSTANTS AT ROOM TEMPERATURE

These values are obtained for $M = \text{Ar}$ from a fit of equation (30) to 58 experimental $k_{\text{obs}}$; the fit had a standard error of $\pm 10\%$.

$K_{3\text{Al}}/\text{mol}^{-1}$
$K_{3\text{AI}}, k_{4\text{Ar}}/\text{mol}^{-2}\text{s}^{-2}$
$K_{3\text{Al}}, k_{4\text{I}}/\text{mol}^{-2}\text{s}^{-2}$
$k_{1\text{Ar}}/\text{mol}^{-1}\text{s}^{-1}$
$k_{2\text{I}}/\text{mol}^{-1}\text{s}^{-1}$
$K_{3\text{Al}}/\text{mol}^{-1}$

3.18 (± 0.63)
3.00 (± 0.16) $\times 10^9$
1.00 (± 0.09) $\times 10^{12}$
0.94 $\times 10^9$
$1.7 \times 10^9$
$6 \times 10^2$

The results of this fit are listed in table 3 along with calculated values for $K_{3\text{Al}}$ and $k_{4\text{I}}$. The latter were obtained by assuming that the steric factor for $k_{4\text{I}}$ (unity) was twice that for $k_{1\text{Ar}}$. The standard error of the fit was $\pm 10\%$; a total of 58 points were fitted. This agreement contrasts with the discrepancies in these results when

they are treated according to (10) (see figure 1). In figure 4, $k_{\text{adj}} = k_{\text{obs}} (1 + K_{3\text{Al}}[\text{Ar}])^2$ is plotted against $\log ([\text{I}_2]/[\text{Ar}])$; the experimental points and the curve represented by the parameters of table 3 are shown. It was not possible to apply this analysis to the data of Bunker & Davidson (1958), since the individual values of $[\text{I}_2]$ and [Ar] were not available.
Calculations were carried out to determine the plausibility of the numerical values of table 3. The value of $k_{4Ar}$ was used to obtain the hard sphere collision diameter for reaction (4). The activation energy was assumed to be zero; a probability factor of 0.5 and an electronic degeneracy factor of $\frac{1}{16}$ for reaction (4) were also assumed. The calculated value, 0.23 nm, is reasonable in view of the approximations made.

The experimental value of $K_{3Ar}$ was applied to expression (24)† to yield the combination of values of well depth, $E$, and equilibrium separation, $R_{eq}$ for the I–Ar interaction, which combination corresponds to the experimental equilibrium constant. These are plotted in figure 5.

Finally, the calculated value of $K_{3I_2}$ was substituted into equation (10), and it was found that the assumption, that $K_{3I_2[I_2]} \ll 1$, is justified over the experimental range of $[I_2]$.

As an additional test, the temperature dependence of $k_{Ar}$ (defined by equation (10) as $k_{Ar} = K_{3Ar} k_{4Ar}$) is predicted by this mechanism. Since reaction (4) is unlikely to have any activation energy, the temperature dependence of $k_{4Ar}$ was assumed to be $T^\frac{1}{2}$. Also the temperature dependence of $K_{3Ar}$ may be determined from equation (24) for any of the ‘suitable’ potentials illustrated by figure 5. The resulting temperature dependence of $k_{Ar}$ for two such I–Ar potentials is shown in figure 6.

† Multiplied by a statistical factor of 2 for heteronuclear molecules, and with $g_M/g_A^2$ replaced by $g_M/g_I = 1$. 

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**Figure 5.** I–Ar Interaction potentials: combinations of $E$ (well depth) and $R_{eq}$ (equilibrium separation) which, on substitution into equation (24)† yield the derived (table 3) value of $K_{3Ar}$. 

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along with available experimental data. Values are scaled relative to the 298 K value given in table 3. This shows that an I–Ar interaction potential 6.3 kJ (1.5 kcal) mol\(^{-1}\) deep with an equilibrium separation of 0.55 nm can account for both the negative temperature dependence of \(k_{Ar}\) and the apparent low concentration ratio fall-off.

The IM mechanism may be further tested by considering its predictions with respect to the four factors treated in the discussion of the I\(_2^*\) mechanism.

![Figure 6: Temperature dependence of \(k_{Ar}\) for two possible I–Ar interaction potentials. The experimental curves are: SCGW, Strong et al. (1957); BD, Bunker & Davidson (1958); PS, Porter & Smith (1961); BDGS, Britton, Davidson, Gehman & Schott (1955).](image)

The first of these involves the plausibility of the internuclear potential required by the intermediate IM species. This interaction potential is some five times deeper than that calculated for van der Waals' forces between argon and xenon (1.25 kJ mol\(^{-1}\); 0.3 kcal mol\(^{-1}\)), which is iodine's neighbour in the periodic table. This appears quite reasonable to us.

Inspection of expression (30) indicates that the fall-off will begin, not at a critical concentration ratio, but at some critical third body concentration; i.e. when \(K_{3M}[M]\) ceases to be negligible compared with unity. Thus for various third bodies, the critical third body concentration \([M]_{dev}\) is proportional to \(1/K_{3M}\). If similar \(I_2\) concentrations are used in all experiments, as was done in the work of Christie et al. (1955), we may therefore write

\[
[[I_2]/[M]]_{dev} \propto K_{3M}.
\]
Furthermore, assuming that $k_{4M}$ will change only slightly for different third bodies $M$, the equation (1) definition of $k_M$ yields

$$\frac{[I_2]/[M]}{d_{ev}} \propto K_{3M} k_{4M} = k_M.$$  

This is the approximate relation noted by Christie (1962). Hence, the IM mechanism correctly predicts the $M$ dependence of $([I_2]/[M])_{dev}$.

The value of $[M]_{dev}$, as stated previously, is proportional to $1/K_{3M}$. As the temperature increases, $K_{3M}$ will decrease; thus $[M]_{dev}$ will increase. Again assuming that similar $I_2$ concentrations are used at all temperatures, this mechanism predicts a decrease in $([I_2]/[M])_{dev}$ with increasing temperature. However, in this case the temperature dependence is relatively small because the potential well of the IA complex is only about 6.3 kJ mol$^{-1}$ deep. Temperature increases from 298 to 323 K or 423 K respectively, would invoke 18% and 50% decreases in $([I_2]/[Ar])_{dev}$, which is well within the experimental uncertainty (see figures 1 and 2).

The final test of the IM mechanism is whether or not it accounts for the discrepancies, shown in figure 1, between experimental values of $k_{obs}$ obtained in different laboratories. A cursory examination of figure 4 shows this to be the case.

The above arguments have shown that taking account of the steady state concentration of IM intermediate is the only way of explaining the low concentration ratios drop-off which agrees with all the experimental observations. In addition, this mechanism explains the observed negative temperature dependence of the experimental rate constants and predicts the depth and minimum position of the IA potential well.

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Note added in proof, 17 November 1969. Christie et al. (1955) have reported room temperature recombination rate constants for each of the other inert gases: He, Ne, Kr, and Xe. These sets of data were fitted in turn to equation (30), with $K_{3I_2} k_{4I_2}$ held fixed at the value given in table 3 (1.0 $\times$ 10$^{12}$ 1$^2$ mol$^{-2}$ s$^{-2}$). The results are presented in table 4, where $k_M = K_{3M} k_{4M}$. There were too few experimental points to allow $K_{3M}$ to be determined with precision, and for $M =$ He and for one of the fits with $M = $ Ne, $K_{3M}$ was arbitrarily set equal to 1.0.
TABLE 4. RATE AND EQUILIBRIUM CONSTANTS AT ROOM TEMPERATURE

FOR M = He, Ne, Kr AND Xe

<table>
<thead>
<tr>
<th>M</th>
<th>$K_{3m}/l^2$ mol$^{-2}$ s$^{-1}$</th>
<th>$10^{-9}k_{3m}/l^2$ mol$^{-2}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>(1.0)</td>
<td>1.0 (± 0.2)</td>
</tr>
<tr>
<td>Ne</td>
<td>(1.0)</td>
<td>1.4 (± 0.2)</td>
</tr>
<tr>
<td></td>
<td>0.1 (± 6.0)</td>
<td>1.3 (± 0.3)</td>
</tr>
<tr>
<td>Kr</td>
<td>7.3 (± 4.6)</td>
<td>4.4 (± 0.5)</td>
</tr>
<tr>
<td>Xe</td>
<td>5.4 (± 2.3)</td>
<td>5.4 (± 0.3)</td>
</tr>
</tbody>
</table>

The results listed in tables 3 and 4 were obtained using the University of Wisconsin Computing Centre nonlinear regression library GASAUS.

REFERENCES