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Measurement of the Absolute Third-order Rate Constant for the Reaction between $Cs+I+He$ by Time-resolved Atomic Resonance Fluorescence Monitoring of Iodine Atoms in the Vacuum Ultraviolet Region $\{I[6s(^2P_J)]-I[5p^5(^2P_{3/2})]\}$ coupled with Steady Atomic Resonance Fluorescence on Atomic Caesium $[Cs(7^2P_J)-Cs(6^2S_{1/2})]$ in the Visible Region

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We present a direct kinetic measurement of the absolute third-order rate constant for the reaction

$$Cs+I+He \rightarrow CsI+He. \quad (1)$$

$I(5^2P_{3/2})$ was generated by the repetitive pulsed irradiation of CsI produced in a flow system from the reaction of CH_3I in the presence of excess atomic caesium derived from a heat-pipe oven. The ground-state iodine atom was monitored by time-resolved atomic resonance fluorescence at $\lambda = 178.3$ nm $\{I[5p^46s(^2P_{3/2})]-I[5p^5(^2P_{3/2})]\}$ using photon counting in the vacuum ultraviolet region. $Cs(6^2S_{1/2})$ was monitored by steady atomic resonance fluorescence of the Rydberg doublet at $\lambda = 457$ nm $[Cs(7^2P_J)-Cs(6^2S_{1/2})]$ using phase-sensitive detection. We report a measured absolute third-order rate constant of $k_1(T=491\text{ K}) = (7.9\pm1.2)\times10^{-31}$ cm^6 atom^{-2} s^{-1}, which we believe to be the first measurement of its kind. We also report an estimate of the rate constant for the reaction

$$I+Cs_2 \rightarrow CsI+Cs \quad (3)$$

of $k_3(T=491\text{ K}) \approx 2\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, which is found to be in accord with previous kinetic measurements on $I+Na_2$ and $Br+K_2$. The crossing between the covalent and the ionic surface, described by the Rittner potential function, is found to take place at 17.3 Å, and hence the recombination is governed by the large impact parameters involved on collision. Consideration of the splitting between the two surfaces, coupled with the Landau-Zener formalism and Monte Carlo calculations of trajectories on those surfaces, yields a good quantitative account of the observed kinetic behaviour, not only of the present recombination measurements but also of shock-tube data that have been reported for the dissociation of CsI at elevated temperatures (2400 K). In view of this, despite the clear third-order kinetic behaviour observed here for reaction (1), detailed theoretical consideration of the 'fall-off' pressure regime found to satisfy both the present measurements and the shock-tube data leads to the preferred value of $k_1(T=491\text{ K}) = 9.1\times10^{-31}$ cm^6 atom^{-2} s^{-1} (±25%). The combination of the recombination and dissociation-rate measurements and the modelling calculations lead to the temperature dependence of the form

$$k_1(491 < T/K < 2400) = 4.1\times10^{-30}T^{-0.24}\text{ cm}^6\text{ atom}^{-2}\text{ s}^{-1}.$$

Measurements of the absolute third-order rate constants for the recombination of two different atoms by direct spectroscopic monitoring of the transient atoms

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themselves have not been reported hitherto on account of various experimental limitations, the most obvious of which concerns the calibrations connecting the spectroscopic signals and the atomic densities. By contrast, in recent years, absolute rate measurements have been described for the bimolecular reactions between atoms such as H, N and O in a flow system with a free radical such as OH.[1] This has been achieved by monitoring of OH under pseudo-first-order kinetic conditions in the time domain in the presence of a calibrated excess of atoms in a flow-discharge system.[1] We have recently presented a series of kinetic measurements between Na, K, Rb or Cs with OH and He[2-5] from which absolute third-order rate constants have been obtained by monitoring $OH(X\ ^2\Pi)$ using time-resolved molecular resonance fluorescence in the pseudo-first-order kinetic regime in the presence of defined excess concentrations of the alkali-metal atoms, derived from a heat-pipe oven, and the third body, helium. In this paper we report an extension of the technique to the study of atomic recombination between Cs + I + He, which we believe is the first measurement of its kind. Not only does this require experimental development for the photochemical generation of the transient iodine atom in a manner significantly different to that for the generation of $OH(X\ ^2\Pi)$[2-5] (see later), and the extension of the time-resolved resonance fluorescence measurements into the vacuum ultraviolet region, but there are also compelling fundamental reasons for the present investigation. As found with Na, K, Rb, Cs + OH + He,[2-5] the interaction between the colliding reactants, Cs + I, on an ionic curve has a dramatic effect on the recombination rate, causing highly efficient recombination.

The interaction between an alkali-metal atom and a halogen atom has been investigated under single-collision conditions in molecular beams; ion-pair formation has been observed[6] for the combinations $Li, Na + I \rightarrow Li^+, Na^+ + I^-$. The theoretical aspects of these reactions have been reviewed by Los and Kleyn.[7] Briefly, collision occurs initially along a covalent surface which, at a critical distance (R_x), is crossed by the ionic diabatic curve describing the ground-state alkali-metal halide molecule. Since one of the covalent surfaces arising from the combination of a ground-state alkali-metal atom ($^2S_{1/2}$) and a halogen atom ($^2P_{3/2}$) is $^1\Sigma^+$ in character, and therefore of the same symmetry as the ionic surface, there is an avoided crossing at R_x described by a splitting ΔE_p between the two adiabatic surfaces in the vicinity of R_x. An adiabatic collision will entail an initial charge transfer at R_x onto the inner ionic section of the adiabatic surface. As the two resulting ions rebound, a charge transfer will occur at R_x, leading to the final separation of the products as atoms, *i.e.* an elastic collision will have occurred. The formation of an ion pair, on the other hand, is caused by electronically non-adiabatic behaviour in the collision at either (but not both) of the points at which the system passes through R_x. The probabilities of such non-adiabatic behaviour at R_x can be estimated using the Landau-Zener formalism,[8] and reaction cross-sections for ion-pair formation can be calculated[9] which agree closely with experiment.[6] Of course, for ion-pair formation to occur, the colliding atoms must have an impact energy greater than the difference between the ionisation energy of the metal atom and the electron affinity of the halogen atom in order for the ions to separate.

Baede[10] has pointed out that the cross-sections for ion-pair formation of the heavier alkali-metal atoms with iodine atoms are very small because one effect of the smaller ionisation energies of the heavier alkali-metal atoms is to yield larger values of R_x. The value of ΔE_p is consequently smaller as a result of a reduced interaction between the wavefunctions of the two atoms. In terms of the probability of adiabatic behaviour, which is proportional to $(\Delta E_p^2)/v$, where ΔE_p is small and v is the relative impact velocity, most collisions between, say, Cs and I will not result in charge transfer except at low impact velocities, which in turn will not provide sufficient translational energy for the ions to separate as products. Thus the probability of inelastic scattering in a crossed-beam experiment will be very low and beyond the range of detection.[10] On the other hand, the recombination of Cs and I atoms in the presence of a bath gas should be a rapid reaction, judging from the measured rates of thermal dissociation of CsI in shock tubes[11] at elevated temperatures, invoking detailed balancing. We have therefore measured the absolute recombination rate of Cs + I + He, which indeed turns out to be very fast. We have performed Monte Carlo calculations to model the reaction rate in an attempt to reconcile our experimental results with the theory of adiabatic covalent-ionic reactions.

EXPERIMENTAL

The immediate experimental objective of the present kinetic measurements is the determination of the pseudo-first-order decay coefficient for the removal of atomic iodine by the reaction

$$\mathrm{Cs+I+He \rightarrow CsI+He} \qquad (1)$$

under conditions where $[\mathrm{Cs}(6\,^2S_{1/2})] \gg [\mathrm{I}(5\,^2P_{3/2})] \ll [\mathrm{He}]$. The experimental procedure follows the kinetic principles described in the analogous investigations on the reaction between Cs + OH + He,[5,12] in which atomic caesium was derived from a heat pipe oven,[5,13] monitored in the flow system by steady atomic resonance fluorescence at $\lambda = 457$ nm $[\mathrm{Cs}(7^2P_J)\text{-}\mathrm{Cs}(6^2S_{1/2})]$ coupled with phase-sensitive detection and where the atomic density in the high-temperature reactor was calculated from the appropriate flow calibrations and the data for the vapour pressure of atomic caesium in equilibrium with liquid caesium at elevated temperatures.[14] Ideally, reaction (1) is most suitably studied by time-resolved resonance-fluorescence measurements on atomic iodine generated from the photolysis of a low equilibrium vapour pressure of CsI in the presence of an excess of caesium, derived from the heat-pipe oven, and the third body, helium. Unfortunately, this photochemical precursor, showing extensive light absorption from the far-ultraviolet to $\lambda \approx 390$ nm,[15] is characterised by a very low equilibrium vapour pressure of 4.2×10^{-7} Torr† at a temperature of 600 K,[16] which represents the ceiling temperature of the present experimental arrangement. This is not governed in this application by the physical constraints of the stainless-steel reactor,[2] which can be used at temperatures in excess of 700 K,[3] but by the background noise level in the photon-counting system using the relevant interference filter for the vacuum ultraviolet (see later). CsI was prepared by the reaction

$$\mathrm{Cs+CH_3I \rightarrow CsI+CH_3} \qquad (2)$$

CF_3I was not used, in order to avoid further reactions yielding CsF. Reaction (2) is presumed to be rapid by analogy with reactions of Na and K with CH_3I [*e.g.* $k(\mathrm{Na+CH_3I}) = (0.7\text{-}2.0) \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}}\ s^{-1}$ at $T = 523$ K].[17] The heat-pipe oven is operated at a temperature of 476 K, where the equilibrium vapour pressure of atomic caesium is 2.1×10^{15} atom $\mathrm{cm^{-3}}$.[14] The reactor itself was kept at a constant temperature of 491 K. The temperatures inside the reactor and the heat-pipe oven were accurately measured by using a movable internal thermocouple. Thus a low concentration of CH_3I, always <10% and usually <2% of the final atomic caesium concentration in the reactor, was introduced into the reactor in a helium flow. It is assumed that all the CH_3I reacts to form CsI. This would be expected to yield a super-saturated vapour of CsI which eventually condenses onto the walls of the reactor and which nucleates in the gas phase. Nevertheless, the finite rate of nucleation and short residence time in the reactor (*ca.* 1-5 s), coupled with replenishment of Cs and CH_3I from the flows, yields monomeric CsI at densities sufficiently high to yield $\mathrm{I}(5\,^2P_{3/2})$ following pulsed

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† 1 Torr = 101 325/760 Pa.

irradiation at concentrations suitable for time-resolved atomic resonance-fluorescence measurements.

The following are the principal atomic transitions of iodine requiring consideration in the present system:[18]

	λ/nm
$I[5p^4 6s(^2P_{3/2})] \rightarrow I[5p^5(^2P^0{}_{3/2})] + h\nu$	178.3
$I[5p^4 6s(^2P_{1/2})] \rightarrow I[5p^5(^2P^0{}_{1/2})] + h\nu$	179.9
$I[5p^4 6s(^2P_{3/2})] \rightarrow I[5p^5(^2P^0{}_{1/2})] + h\nu$	206.2

and which are readily observed by time-resolved atomic absorption spectroscopy or by plate photometry following photolysis of alkyl iodides such as CF_3I and CH_3I.[19-21] The atomic emission resonance source employed a microwave discharge through iodine and a small pressure of helium in a sealed quartz lamp, as described by Deakin and Husain[22,23] following Liuti and Mentall.[24] The end window of this spectroscopic source was constructed of high-purity Spectrosil quartz ($\lambda >$ *ca.* 160 nm), as were the lenses and optical components in the detection system. In view of our principal concern with the transition at $\lambda = 178.3$ nm for the kinetic study of the ground-state iodine atom, the optical path between the spectroscopic source and optical entry port to the reactor[2] was flushed with nitrogen contained by means of an appropriately constructed plastic bag.[25,26] This enjoys the advantage of permitting adjustment of the lens system within the bag for optimising the vacuum ultraviolet resonance-fluorescence signal.

The photomultiplier tube (E.M.I. 9816 QB), incorporating a Spectrosil end window, and the associated electronics for photon counting of the resonance-fluorescence signals were those described in previous studies.[5,12] The broad-band interference filter for optical separation employed here (Acton Research Corporation, U.S.A.) is characterised as follows: peak transmission (15.2%) at $\lambda = 176.5$ nm; band width at half-peak transmission = 20.8 nm. Simple considerations based on these characteristics indicate that the transmission at $\lambda = 178.3$ nm is *ca.* 13.9%, that at $\lambda = 179.9$ nm is *ca.* 12.7%, and that at $\lambda = 206.2$ nm is barely significant. Full details of the use of the flow system, the high-temperature reactor, the pulsed initiation source by discharge through N_2 at atmospheric pressure and the data processing of the resonance-fluorescence signals may be found in earlier papers.[2-5,12] The low photon counts observed in the kinetic decays clearly justify the neglect of radiation trapping and the assumption of a linear relationship between fluorescence intensity and concentration of atomic iodine. All materials (Cs metal, He, N_2, CH_3I and CF_3I) were essentially prepared as described in previous papers.[5,12,20,27]

RESULTS AND DISCUSSION

KINETIC RESULTS

Fig. 1(*a*) gives an example of the digitised time-variation of the light intensity at $\lambda = 178.3$ nm (with a minor component at $\lambda = 206.2$ nm), indicating the decay of the time-resolved resonance fluorescence from $I(5\,^2P_{3/2})$ following the pulsed irradiation of a low pressure of CF_3I in the presence of an excess of helium buffer gas and *ca.* 10 mTorr O_2, added in order to relax collisionally the $I(5\,^2P_{1/2})$ formed from the photolysis of CF_3I.[27] The atomic resonance-fluorescence signals [*e.g.* fig. 1(*a*)] can be seen to be satisfied by the form

$$I_F = \theta_1 + \theta_2 \exp(-k't) \qquad \text{(i)}$$

where θ_1 represents the steady scattered light from the resonance lamp and k' the overall first-order coefficient for the decay of the atom. All the decay curves were subjected to fitting to eqn (i) using the LAMFIT procedure of Powell.[28] The genuine resonance fluorescence signal due to the decay of $I(5\,^2P_{3/2})$ can be identified with

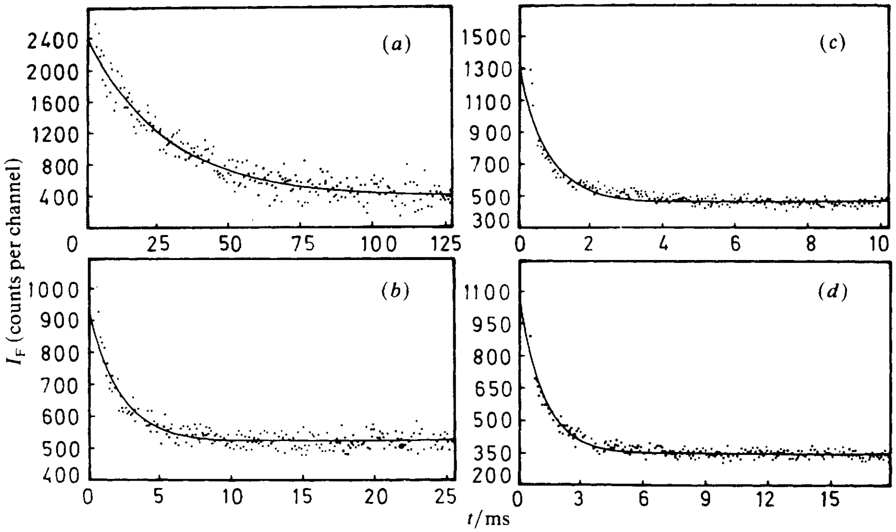

Fig. 1. Digitised time-variation of the light intensity at $\lambda = 178.3$-206.2 nm $\{I[6s(^2P_J)]$-$I[5p^5(^2P_J)]\}$ indicating the decay of time-resolved atomic iodine fluorescence (I_F, counts per channel) following the pulsed irradiation of CsI vapour resulting from the reaction of CH_3I and an excess of atomic Cs derived from a heat-pipe oven and monitored in the steady mode using atomic resonance fluorescence at $\lambda = 457$ nm $[Cs(7\,^2P_J)$-$Cs(6\,^2S_{1/2})]$ coupled with phase-sensitive detection. [Cs] = [Cs] (initial)-[CH_3I] (initial); $T = 491$ K; $E = 45$ J; repetition rate = 1 Hz; no. of individual experiments = 256; (–) $I_F = \theta_1 + \theta_2 \exp(-k't)$.

	$[Cs]/10^{14}$ atom cm^{-3}	$[He]/10^{17}$ atom cm^{-3}
(*a*)	($[CF_3I] = 4 \times 10^{15}$ molecule cm^{-3})	15
(*b*)	1.9	14.5
(*c*)	8.1	14.5
(*d*)	8.1	4.9

the second term on the right-hand side of eqn (i) and can be expressed in the form:[14]

$$I_F = \frac{\phi[I(5\,^2P_{3/2})]_{t=0} \exp(-k't)}{1 + k_Q[Q]/A_{nm}} \qquad \text{(ii)}$$

where the symbols have their usual meaning. The presentation of fig. 1(*a*) is primarily intended to illustrate the nature of the signal and its long-lived quality reflecting removal of the atom by diffusion. Decays of $I(5\,^2P_{3/2})$ in helium at a variety of temperatures have been measured and demonstrate the role of this removal process in the absence of Cs, showing particularly that such rates are very slow, typically factors of 10^2-10^3 slower than in the presence of atomic caesium.

Fig. 2 shows the variation of k' derived from computerised fitting of the atomic resonance fluorescence decay traces according to eqn (i) following the pulsed irradiation of CF_3I + He, in the presence of small quantities of 0_2, as a function of the reciprocal of the pressure of helium at $T = 300$, 380, 490 and 600 K. Thus the combination of eqn (i) and (ii) describes the decay of the fluorescence intensity of the transition at $\lambda = 178.3$ nm, and fig. 2 therefore represents diffusional removal of

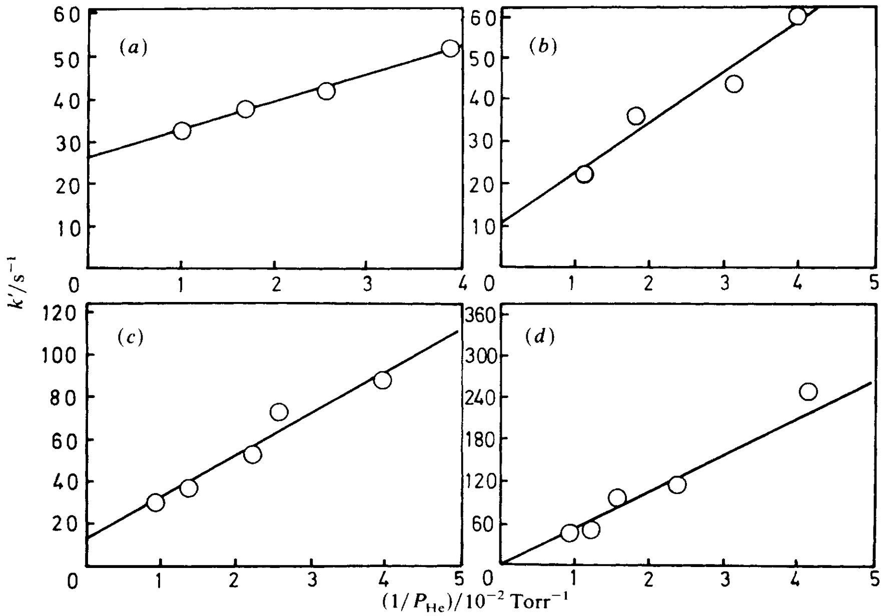

Fig. 2. Variation of the pseudo-first-order rate coefficient, k', for the overall decay of $I(5\,^2P_{3/2,1/2})$ as a function of the reciprocal of the pressure of helium, and at different temperatures, with monitoring by time-resolved atomic resonance fluorescence at $\lambda =$ 178.3-206.2 nm $\{[6s(^2P_J)]\text{-}I[5p^5(^2P_J)]\}$ following the pulsed irradiation of CF_3I, demonstrating diffusional loss, T/K: (*a*) 300, (*b*) 380, (*c*) 490 and (*d*) 600.

$I(5\,^2P_{3/2})$ in He at these temperatures. It is not our intention to present a detailed study of diffusion coefficients of atomic iodine in this paper, especially in the absence of detailed definition of the boundary conditions necessary for quantitative solution of the diffusion equation.[29,30] Nevertheless, the slopes of the plots in fig. 2 yield estimates for $D[I(5\,^2P_{3/2})\text{—}He]$ in sensible accord with the range of values reported for $D[I(5\,^2P_{1/2})\text{—}He]$.[19,31] Fig. 2, in particular part (*c*), for $T = 490$ K, the temperature of the present measurements on reaction (1), show diffusional removal to be very slow, as low as 30 s^{-1}, and hence only a very small correction will be required for this mode of removal when decay coefficients are characterised for $I(5\,^2P_{3/2})$ in the presence of Cs + He.

Fig. 1(*b*) and (*c*) give examples of the time-resolved atomic iodine resonance fluorescence signals following the pulsed irradiation of CsI in the presence of defined excess concentrations of atomic caesium, derived from the heat-pipe oven, and the helium buffer gas at $T = 491$ K. Fig. 1(*b*) and (*c*) demonstrate atomic iodine decay profiles for varying [Cs] and constant [He], and fig. 1(*c*) and (*d*), profiles for varying [He] and fixed [Cs]. The phytolysis of CsI in the region $\lambda \approx 300\text{-}390$ nm yields primarily $Cs(6\,^2S_{1/2})$ and $I(5\,^2P_{3/2})$,[15] with the production of $I(5\,^2P_{1/2})$ and electronically excited Cs atoms at lower wavelengths. The latter will be removed by spontaneous atomic emission during the pulsed initiation process, and we may reasonably expect efficient and rapid quenching of $I(5\,^2P_{1/2})$ by CsI by analogy with other iodides.[19] Hence the decays in traces of the type presented in fig. 1(*b*) and (*c*) may be attributed to $I(5\,^2P_{3/2})$ monitored *via* the resonance transition at $\lambda = 178.3$ nm.

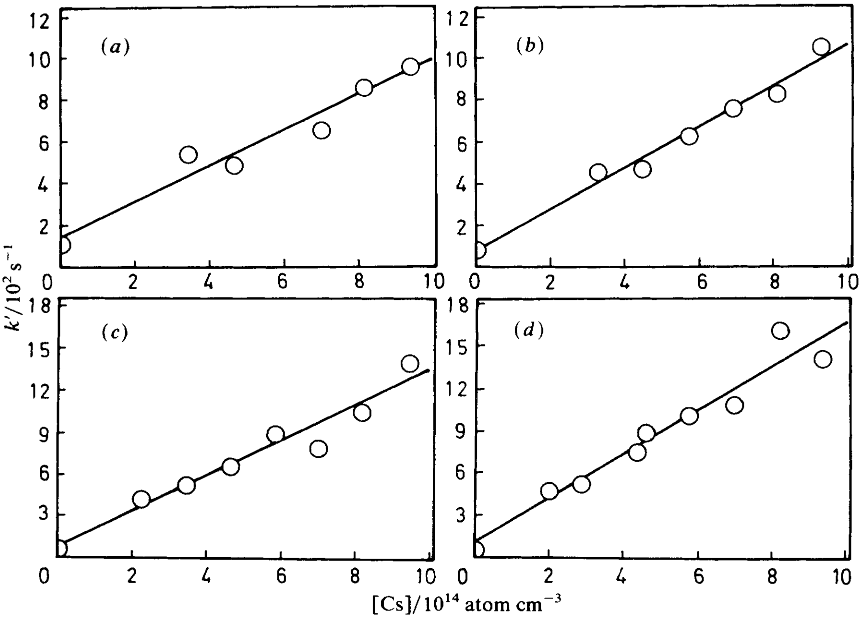

Fig. 3. Variation of the pseudo-first-order rate coefficient, k', for the decay of $I(5\,^2P_{3/2})$, obtained by time-resolved atomic resonance fluorescence at λ = 178.3 nm $\{I[6s(^2P_{3/2})]-I[5p^5(^2P_{3/2})]\}$ following the pulsed irradiation of CsI vapour in the presence of different concentrations of atomic caesium, monitored in the steady mode using atomic fluorescence of the resonance transition at λ = 457 nm $[Cs(7\,^2P_J)-Cs(6\,^2S_{1/2})]$ coupled with phase-sensitive detection (T = 491 K). $[He]/10^{17}$ atom cm^{-3}: (a) 4.9, (b) 6.9, (c) 10.4 and (d) 14.5.

Fig. 3 shows the variation of k' for the decay of $I(5\,^2P_{3/2})$ obtained by computerised fitting of the raw data to eqn (i), as a function of the concentration of atomic caesium for different concentrations of helium. The concentration of atomic caesium in the reactor was varied by a factor of *ca.* five by control of the flows for each of the five different total pressures of He employed in the range 24.3–83.4 Torr, four of which are presented in fig. 3. The atomic caesium concentration for each data point in this figure was calculated by subtracting the small concentration of CH_3I in the flow from the initial concentration of Cs calculated from the combination of the equilibrium vapour density in the heat pipe coupled with the ratio of flows mixing in the reactor. On average, this correction was of the order of 3%.

The overall first-order coefficient, k', for the decay of $I(5\,^2P_{3/2})$, arising from the combination of the third-order reaction (1) and removal by diffusion is given by the form

$$k' = k_{\text{diff}} + k_1[\text{Cs}][\text{He}]. \qquad \text{(iii)}$$

Thus the resulting plot of the slopes of the plots given in fig. 3(a)–(d), namely $k_2' = (k' - k_{\text{diff}})/[\text{Cs}]$ against [He], should be linear and of slope k_1, the absolute third-order rate constant for reaction (1). The result is shown in fig. 4. This plot is linear within experimental error, yielding a value of $k_1(T = 491\text{ K}) = (7.9 \pm 1.2) \times 10^{-31}$ cm^6 $atom^{-2}$ s^{-1}. As with previous measurements of third-order rate constants for reactions undergone by alkali-metal atoms derived from a heat-pipe oven,[2-5] the quoted error of 15% in k_1 primarily arises not from scatter in the kinetic data, but from the control of the temperature in the heat-pipe oven and the resulting uncertainty in the equilibrium atomic vapour density.

Unlike the investigations on the rates of the analogous third-order reactions between Na, K, Rb, Cs+OH+He,[2-5] the intercept in fig. 4 is significant, namely, 4.3×10^{-13} cm^3 atom^{-1} s^{-1}. We believe this intercept reflects the reaction of $I(5\,^2P_{3/2})$ with the dimer Cs_2:

$$I(5\,^2P_{3/2})+Cs_2 \rightarrow CsI+I. \tag{3}$$

Assuming Cs and Cs_2 to be in equilibrium:

$$2Cs \xrightleftharpoons{K_{eq}} Cs_2 \tag{4}$$

then k' should be given by the form:

$$k'=k_{diff}+k_1[Cs][He]+k_3K_{eq}[Cs]^2. \tag{iv}$$

No obvious curvature, as indicated by computerised parabolic curve fitting to plots of the type given in fig. 3, was apparent. It is proposed that the small degree of curvature is hidden within the error of the plots of fig. 3; indeed, this type of procedure has been the means of estimating the rate constants or upper limits for reaction of OH with Na_2, K_2, Rb_2 and Cs_2 previously[2-5] and the value for k_3 obtained here supports the assumption. Since the range of concentrations of Cs employed in the five sets of plots at different pressures of He (fig. 3) was the same in each case, the effect will yield an overestimate of the slope of k_2' against [Cs] of magnitude approximately given by $k_3K_{eq}[Cs]_{max}$, where $[Cs]_{max}$ is the maximum concentration of Cs used in the present measurements, namely, 9.4×10^{14} atom cm^{-3}. This constant overestimate appears in the intercept of the plot of fig. 4. Hence we may calculate K_{eq} for $T=491$ K (1.8×10^{-16} cm^3 molecule^{1-})[13] and finally estimate $k_3\approx 2\times10^{-10}$ cm^3 molecule^{-1} s^{-1}. This may be compared with the analogous values of $k(I+Na_2,\ T=573\ K)=1.0\times10^{-10}$ cm^3 molecule^{-1} s^{-1} derived from diffusion-flame measurements[32] and $k(Br+K_2,\ T=491\ K)\approx5\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, which we have estimated from the reported cross-sections (90 Å^2) derived from a molecular-beam study.[33] Thus the intercept in fig. 4 is sensibly consistent with the removal of $I(5\,^2P_{3/2})$ by reaction (3).

Phenomenologically, the value of k_1 of 7.9×10^{-31} cm^6 atom^{-2} s^{-1} is strikingly large compared with many recombination rate constants for atomic iodine involving other I atoms or diatomic molecules [*e.g.* $k(I+I+He,\ T=491\ K)=1.8\times10^{-33}$ cm^6 atom^{-2} s^{-1};[34] $k(I+NO+He,\ T=310\ K)=6.04\times10^{-33}$ cm^6 atom^{-2} s^{-1} [35]]. However, we may immediately compare our result with that described by Luther *et al.*[11] for the thermal dissociation rate derived from shock-tube measurements at $T=2400$ K. Those authors[11] report a branching ratio at this elevated temperature of 70% of the molecules dissociating to form atoms and 30% into ions. Combining their reported dissociation rate constant of 5.8×10^{-16} cm^3 molecule^{-1} s^{-1} with a calculated equilibrium constant of 4.0×10^{-16} cm^3 molecule^{-1} [36] for the equilibrium

$$CsI \rightleftharpoons Cs+I \tag{5}$$

yields an estimate for the recombination rate constant ($T=2400$ K, $[Ar]=1.2\times10^{19}$ atom cm^{-3}) of 2.4×10^{-31} cm^6 atom^{-2} s^{-1}. Thus, our value of $k_1(T=491\ K)$ is of the same order of magnitude as this estimate. However, the shock-tube data showed, very unusually for a diatomic dissociation process, that for the pressure regime in which the measurements were carried out, the dissociation rate of CsI lay well into

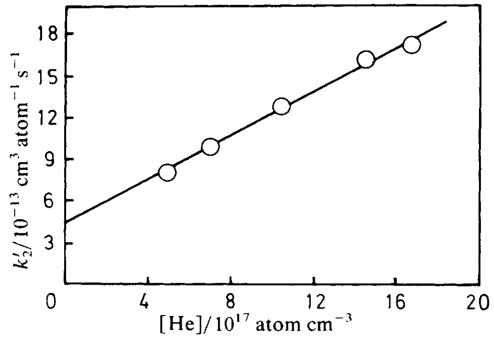

Fig. 4. Variation of the pseudo-second-order rate coefficient, $k_2'\{=(k'-k_{\mathrm{diff}})/[\mathrm{Cs}(6\,^2S_{1/2})]\}$ for the decay of $\mathrm{I}(5\,^2P_{3/2})$ as a function of the atomic helium concentration obtained by time-resolved atomic resonance fluorescence at $\lambda = 178.3$ nm$\{\mathrm{I}6s(^2P_{3/2})]-\mathrm{I}[5p^5(^2P_{3/2})]\}$ following the pulsed irradiation of CsI vapour, with monitoring of atomic caesium by steady fluorescence at $\lambda = 457$ nm $[\mathrm{Cs}(7\,^2P_J)-\mathrm{Cs}(6\,^2S_{1/2})]$ coupled with phase-sensitive detection ($T = 491$ K).

the fall-off region, being between first and zeroth order with respect to the concentration of the bath gas. Thus we cannot use this high-temperature estimate in conjunction with our own value for k_1 at $T = 491$ K to obtain an estimate of the temperature dependence of the recombination rate constant in the low-pressure limit. In the next section we perform detailed calculations to explain quantitatively both the very large recombination rate constant that we have measured and also the observation of the fall-off from the low-pressure limit of this reaction at unusually low pressures of the bath gas.

POTENTIAL CURVES

Fundamental consideration of the recombination between Cs + I must be formulated in terms of the potential curves involved in reaction, and these have been the subject of extensive and detailed spectroscopic and theoretical discussion.[37] It has clearly been established[37] that CsI exists in the gas phase as an ion pair on a $^1\Sigma^+$ surface. This surface is illustrated in fig. 5, namely surfaces I–III, which we have calculated using the full Rittner potential function[38] with the parameters listed in table 1. This surface has been shown[37] to be an accurate representation of the ionic diabatic surface of an alkali-metal halide, and is given by the standard form:

$$V_1(r) = -r^{-1} + A\exp(-r/\rho) - C_6/r^6 - (\alpha_+ + \alpha_-)/2r^4 - 2\alpha_+\alpha_-/r^7 \qquad \text{(v)}$$

where α_+ and α_- are the ion polarisibilities,[39-41] and the factor C_6 is calculated using the standard Slater–Kirkwood approximation.

The second surface depicted in fig. 5, i.e. II–IV, is a ground-state covalent diabatic surface representing the interaction between $\mathrm{Cs}(6\,^2S_{1/2})$ and $\mathrm{I}(5\,^2P_{3/2})$ atoms, and has been calculated using the expression

$$V_2(r) = A\exp(-r/\rho) - C'_6/r^6. \qquad \text{(vi)}$$

The accurate nature of this surface is not required for the detailed calculations (see later), and is included in fig. 5 for purposes of discussion only. The polarisibilities of the atoms are taken from ref. (39)–(41).

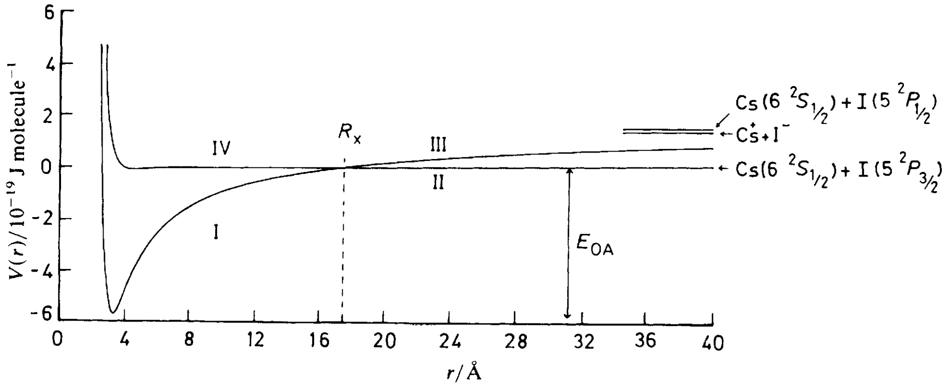

Fig. 5. Diabatic potential curves representing the interaction between $Cs^+ + I^-$(I and III) and $Cs(6^2S_{1/2}) + I(5^2P_{3/2})$ (II and IV). R_x = pseudo-crossing-point of the diabatic curves; E_{0A} = dissociation energy of CsI to $Cs(6\,^2S_{1/2}) + I(5\,^2P_{3/2})$.

Table 1. Parameters for the Rittner model and the covalent surface

	Rittner model	
$D_0 = 3.56$ eV	$\nu_e = 119.18$ cm^{-1}	$B_e = 0.0236$ cm^{-1}
$r_e = 3.3152$ Å		
$\alpha_{Cs^+} = 2.27$ Å^3	$\alpha_{I^-} = 7.44$ Å^3	$C_6 = 2.7 \times 10^{-17}$ J Å^6
repulsive term: $A \exp(-r/\rho)$,	$A = 5.76 \times 10^{-15}$ J	$\rho = 0.31$ Å
	covalent surface	
$\alpha_{Cs} = 59.6$ Å^3	$\alpha_I = 3.9$ Å^3	$C_6' = 8.2 \times 10^{-17}$ J Å^6

The CsI molecule either dissociates adiabatically to atoms, $Cs(6\,^2S_{1/2})$ and $I(5\,^2P_{3/2})$, which involves a charge-transfer process, or dissociates diabatically to ions. Conversely, recombination of the atoms along the adiabatic potential surface II–I involves a change in electronic structure at $R_x = 17.3$ Å, the closest point of approach of the two adiabatic curves I–II and III–IV. This may alternatively be viewed as the point where the two diabatic surfaces, *i.e.* the $^1\Sigma^+$ covalent surface II–III and the $^1\Sigma^+$ ionic surface I–IV, exhibit an avoided crossing on account of like symmetry.[37] The size of the splitting between the two adiabatic surfaces at R_x, ΔE_p, is in fact very small in the case of CsI, because the interaction between orbitals on the Cs and I atoms is reduced at such a large distance of R_x. Grice and Herschbach[42] have produced estimates of ΔE_p for all the alkali-metal halide pairs. Their calculation is based on a solution of a 2×2 secular equation derived from mixing the diabatic ionic and covalent basis states, which are simply approximated by asymptotic wavefunctions. In the case of CsI, the splitting between the adiabatic surfaces, ΔE_p, is estimated to be *ca.* 4×10^{-24} J molecule^{-1}.[42]

We may also obtain an estimate of ΔE_p from the experimental dissociation rate constant of CsI measured by Luther *et al.*[11] in the following manner. If P is the probability of adiabatic behaviour along the surface I–II during dissociation or recombination, then according to the simplified Landau-Zener formula,[8,43]

$$P = 1 - \exp(-K/v) \qquad \text{(vii)}$$

where $K = \pi^2(\Delta E_p{}^2 R_x{}^2)/(\boldsymbol{h}e^2)$ and $v = (2E/\mu)^{1/2}$, E is the relative translational energy and the other symbols have their standard meaning. During molecular dissociation, the average probability of adiabatic dissociation is calculated by averaging P across vibrational energy levels greater in energy than the threshold energy, E_{0A}, with the distribution function $f(E)\,dE = \exp(-E/\boldsymbol{k}T)\,d(E/\boldsymbol{k}T)$. This gives

$$\bar{P}_{\text{vib}} = \pi^2 \Delta E_p{}^2 R_x{}^2/(\boldsymbol{h}e^2)(\pi\mu/2\boldsymbol{k}T)^{1/2}. \qquad \text{(viii)}$$

Dissociation can be achieved by a trajectory along either the I-II or the II-IV-III surface. This introduces a factor of two into an expression for the limiting high-pressure dissociation rate constant, namely[44]

$$k_{\text{diss},\infty} = 2\nu\bar{P}Q\ddagger/Q \exp(-E_{0A}/\boldsymbol{k}T) \qquad \text{(ix)}$$

where ν is the vibrational frequency of the molecule at E_{0A} and $Q\ddagger$ and Q are the partition functions of a dissociating molecule at the threshold energy, and one that is thermally averaged, respectively. Substituting eqn (viii) into eqn (ix) and evaluating the partition functions one derives

$$k_{\text{diss},\infty} = \nu_e(R_x/R_e)^2 R_x{}^2(\pi\mu/2\boldsymbol{k}T)^{1/2} 2\pi^2/(\boldsymbol{h}e^2)\Delta E_p{}^2 \exp(-E_{0A}/\boldsymbol{k}T) \qquad \text{(x)}$$

where ν_e is the fundamental frequency and R_e is the equilibrium bond distance. [This expression for $k_{\text{diss},\infty}$ is quoted in ref. (11)]. The dissociation rate constant reported by Luther *et al.*[11] did not quite reach the high-pressure limit; in fact, those authors observed $k_{\text{diss},\infty} \propto [\text{M}]^{0.3}$, but using their experimental value for the dissociation rate together with eqn (x) one can estimate $\Delta E_p = 5.0 \times 10^{-23}$ J molecule^{-1}. This result is very close to the estimate of Grice and Herschbach,[42] bearing in mind the extremely small splitting of the adiabatic states and the crudeness of the method of estimation. We employ our calculated value of $\Delta E_p = 5.0 \times 10^{-23}$ J molecule^{-1} in the calculations that follow.

Considering now the recombination of Cs and I atoms, the average probability of adiabatic collisions, *i.e.* along II-I, can be estimated by averaging P over thermal impact energies and noting that a trajectory along either the II-I or the II-IV-III surface will produce an ion pair. The probability of charge transfer occurring upon an impact of a Cs and I atom with an impact parameter $< R_x$ is thus estimated to be 0.0029. This low probability is reflected experimentally in the negligible cross-sections that have been observed for the collisional ionisation process of $\text{Cs} + \text{I} \rightarrow \text{Cs}^+ + \text{I}^-$ in molecular beams.[9]

MONTE CARLO CALCULATION OF THE RATE CONSTANT FOR Cs+I+He

In order to model the recombination reaction between Cs and I atoms we will assume the energy-transfer process dominates with He as the bath gas according to the mechanism

$$\text{Cs} + \text{I} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} (\text{Cs}^+\text{I}^-)^* \xrightarrow{k_7[\text{M}]} \text{CsI}. \qquad (6)$$

When a Cs($6\,^2S_{1/2}$) atom approaches an I($5\,^2P_{3/2}$) atom, eight molecular states will be produced (only one of which is $^1\Sigma^+$) which can interact with the ground ionic state of CsI of the same symmetry. This would generally introduce a statistical factor into a calculation of the recombination rate constant. In the present case, however, little is known of the nature of the atomic coupling at such a large interatomic distance as R_x, where these covalent states are crossed by the ionic $^1\Sigma^+$ state [see chap. 3 of ref. (37)]. Furthermore, since near the critical distance R_x all eight states will be degenerate, there may be very rapid transitions between curves either spontaneously, or because of perturbations arising from the proximity of a third body, on the time-scale of the approaching Cs and I atoms. This is discussed in some detail in ref. (45). We therefore prefer to assume an electronic factor of unity, which appears to be justified by the agreement between calculation and experiment (see below).

If we assume that reaction will only take place if a given trajectory follows the II-I or II-IV-III surfaces to form a CsI ion pair, and that no reaction results from recombination on the eight covalent surfaces which are only slightly bound,[37] k_6 and k_{-6} are clearly dependent on the probability of adiabatic behaviour at the crossing point, R_x. Considering the excited ion pair CsI* to be in steady-state,

$$k_{\text{rec}} = \frac{k_6 k_7[\text{M}]}{k_{-6} + k_7[\text{M}]}. \tag{xi}$$

Thus, at the limit of low pressure,

$$k_{\text{rec},0} = k_6 k_7 / k_{-6}. \tag{xii}$$

k_7 can be expressed as $\beta_c Z$,[46] where Z is the collision frequency of the third body and CsI* and β_c is the collision efficiency of the third body which takes account of weak collisions that do not effectively remove sufficient energy to stabilise CsI* on every collision.

Thus the overall rate constant for recombination may be written as

$$k_{\text{rec},0} = \beta_c Z K_6(T) \tag{xiii}$$

where $K_6(T)$ is the equilibrium constant for reaction (k_6/k_{-6}). We now calculate the equilibrium constant $K_6(T)$ using the dynamic method of Bunker[45,47] and incorporating the recent work of Smith.[48]

Smith[48] noted that k_{-6}, k_6 and k_7 [$=Z$ in the strong-collision approximation, when $k^{\text{sc}}{}_{\text{rec},0} = ZK_6(T)$ may all depend on the impact energy E and impact parameter b of a particular collision, and one should therefore begin by defining a detailed rate coefficient for the moment at the strong-collision approximation:

$$k_{\text{rec},0}(E, b) = Pr(E, b) Z(E, b) k_6(E, b) / k_{-6}(E, b) \tag{xiv}$$

and proceed to find a thermal rate constant by appropriate integrations over the spread of E and b values. The probability factor $Pr(E, b)$ takes account of weak-collision effects and their dependence on E and b. Following Smith[48] we make the assumption that Z is independent of E and b and that any dependence of k_7 on E and b is reflected entirely in the values of the probability factors $Pr(E, b)$. The rate constants $k_6(E, b)$ and $k_{-6}(E, b)$ can be written as the products of the probability of an adiabatic reaction occurring at energy E, $P(E)$, and rate constants $k_6'(E, b)$ and $k_{-6}'(E, b)$, which we can calculate having assumed a probability of adiabatic behaviour of unity, *i.e.* $k_6(E, b) = k_6' P(E)$ and $k_{-6}(E, b) = k_{-6}'(E, b) P(E)$. Thus in the low-pressure limit the recombination rate constant, $k_{\text{rec},0}$, is independent of the probability of adiabatic behaviour and may be calculated by assuming that every collision of Cs and I with an impact parameter $<R_x$ will result in formation of an excited ion pair, *i.e.*

$$k_{\mathrm{rec},0}(E,b) = Pr(E,b)Zk_6'(E,b)/k_{-6}'(E,b). \tag{xv}$$

Then

$$k_{\mathrm{rec},0}(T) = Z\int_0^{\infty}\int_0^{b_{\max}} Pr(E,b)k'_6(E,b)/k'_{-6}(E,b)\,\mathrm{d}b\,\mathrm{d}E. \tag{xvi}$$

Adopting the dynamic approach of Bunker,[45] which is based on the equation

$$\tfrac{1}{2}\mu\dot{r}^2 = E(1-b^2/r^2) - V \tag{xvii}$$

the lifetime of one vibrational period of a complex of defined collision energy E, reduced mass μ, and impact parameter b, can be expressed as

$$\tau(E,b) = (\mu/2)^{1/2}[E(1-b^2/r^2)-V]^{-1/2}\,\mathrm{d}r, \qquad [=1/k_{-6}'(E,b)] \tag{xviii}$$

where the potential energy V is a function of r, the separation of the two nuclei. In the present case, $V(r)$ is very adequately given by the Rittner surface (see above). Here we have assumed that the CsI* ion-pair complex is formed by a pair of colliding atoms with an impact parameter $b<17.3$ Å (*i.e.* R_x). In the case of the Rittner surface the long-range potential is r^{1} in character, owing to simple Coulomb attraction. The effective potential of a particular trajectory is given by

$$V_{\mathrm{eff}}(r) = V(r) + Eb^2/r^2 \tag{xix}$$

and it will be noted that, unlike the case examined by Smith[48] in which the long-range interatomic forces were dispersive and gave rise to a r^{-6} potential, there are no centrifugal barriers in the present instance. This effect is illustrated in fig. 6, which shows the Rittner surface as well as three effective potentials arising from the same impact energy E, but different impact parameters b. There is a slight maximum in the effective potential at R_x which is the result of the change in nature of the adiabatic surface from being ionic to becoming covalent. Thus the integration limits of eqn (xviii) can be seen to be $r_{\max} = R_x$ and $r_{\min}$ = the turning point on the inner branch of the effective potential curve. $r_{\max}$ is therefore independent of the nature of the trajectory, but $r_{\min}$ is a function of E and b. $k_6'(E,b)$ is only zero if $b>R_x$. Otherwise,

$$k_6'(E,b) = 2\pi b(2E/\mu)^{1/2}f(E) \tag{xx}$$

where $f(E)$ is now a normalized function describing the distribution of collision energies at temperature T. Furthermore, $\tau(E,b)$ is twice the time obtained by integrating the right-hand side of eqn (xviii) between $r_{\max}$ and $r_{\min}$.

Combining eqn (xvi), (xviii) and (xx) yields the following expression for $k_{\mathrm{rec},0}(T)$:

$$\begin{aligned} k_{\mathrm{rec},0}(T) &= \beta_c k^{\mathrm{sc}}{}_{\mathrm{rec},0}(T) \\ &= \beta_c Z\int_0^{\infty}\int_0^{b_{\max}} E^{1/2}f(E)2\pi b\left(2\int_{r_{\min}}^{r_{\max}}[E(1-b^2/r^2)-V]^{-1/2}\,\mathrm{d}r\right)\mathrm{d}b\,\mathrm{d}E. \end{aligned} \tag{xxi}$$

The maximum impact parameter $b_{\max}$, is R_x. Any trajectory with an impact parameter $>R_x$ will not lead to an adiabatic reaction along II–I.

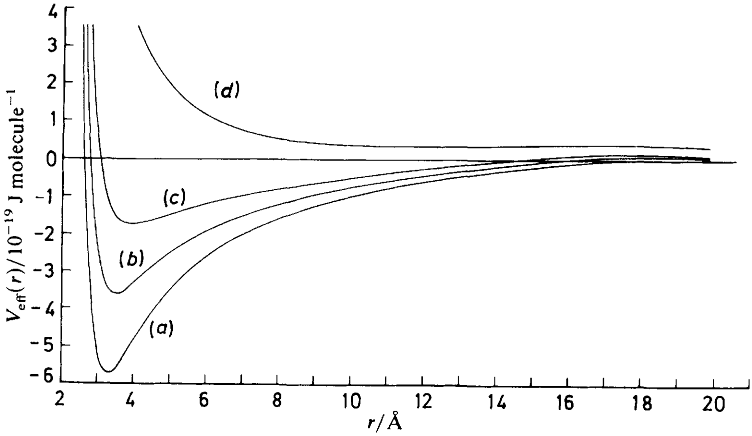

Fig. 6. Potential curves showing the effective interaction for adiabatic collisions between $Cs(6\,^2S_{1/2})+I(5\,^2P_{3/2})$ at constant impact energy ($E=5\times10^{-20}$ J molecule^{-1}) and varying impact parameter (b). b/Å: (a) 0, (b) 7, (c) 10 and (d) 15.

Table 2. Monte Carlo calculations

$\sigma_{CsI}=5.62$ Å　　$\varepsilon/k_{CsI}=1880$ K

$\sigma_{CsI\text{-}He}=4.09$ Å　　$\varepsilon/k_{CsI\text{-}He}=139$ K

$T=491$ K

$Z_{LJ}=9.1\times10^{-10}$ cm^3 molecule^{-1} s^{-1}

$K_6(T)=k_6/k_{-6}=1.0\times10^{-20}$ cm^3 molecule^{-1}

$k^{sc}{}_{rec,0}=9.1\times10^{-30}$ cm^6 molecule^{-2} s^{-1}

assuming $\beta_c=0.1$,

$k_{rec,0}=9.1\times10^{-31}$ cm^6 molecule^{-2} s^{-1}

$T=2400$ K

$Z_{LJ}=1.42\times10^{-9}$ cm^3 molecule^{-1} s^{-1}

$K_6(T)=1.83\times10^{-20}$ cm^3 molecule^{-1}

$k^{sc}{}_{rec,0}=2.6\times10^{-29}$ cm^6 molecule^{-2} s^{-1}

assuming $\langle\Delta E\rangle$ constant with T, $\beta_c=0.025$

$k_{rec,0}=6.2\times10^{-31}$ cm^6 molecule^{-2} s^{-1}

Following the method of Smith,[48] we have used a Monte Carlo method to evaluate eqn (xxi) at $T=491$ and 2400 K after making suitable substitutions.[48] Values of E and b are chosen by well established pseudo-random techniques.[47] The results of the calculations of $K_6(T)$ and the strong-collision rate constant at the two temperatures are given in table 2. The calculation of the Lennard-Jones' collision frequency between CsI + He is carried out using the expression given in ref. (46). The Lennard-Jones' parameters, σ_{CsI-He} and ε/k_{CsI-He}, are estimated[2] from boiling-point and density measurements.[49,50] It will be observed that at $T = 491$ K the ratio $k_{\text{exptl}}/k^{\text{sc}}_{\text{rec,0}}$ is 0.08 ± 0.01, which is very much in accord with the expected collision efficiency of He at this temperature, where $\beta_c \approx 0.1$. This corresponds to an average energy transferred upon collision, $\langle \Delta E \rangle = -466$ J mol^{-1}.[46,51-53]

The strong-collision recombination rate constant at $T = 2400$ K is shown in table 2. In order to estimate the collision efficiency of He at this temperature, and hence the weak-collision rate constant, we take a value for β_c at $T = 491$ K and extrapolate to $T = 2400$ K using the relation derived by Tröe:[46]

$$\frac{\beta_c}{1 - \beta_c^{1/2}} = \frac{-\langle \Delta E \rangle}{F_E \boldsymbol{R} T}. \qquad \text{(xxii)}$$

(In the case of a diatomic molecule the energy dependence of the density of states, F_E, is unity.) We assume, with some experimental justification,[51] that $\langle \Delta E \rangle$ is approximately independent of temperature. The collision efficiency at $T = 2400$ K is then 0.025, yielding

$$k_{\text{rec,0}} = 6.6 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}.$$

This calculation indicates that there is only a very slight negative temperature dependence of $k_{\text{rec,0}}$. In terms of the reaction dynamics this can be seen to be due to the lack of a centrifugal barrier in the effective potential governing these trajectories. If the long-range attractive part of the potential was such that centrifugal barriers were present, then at the large impact energies associated with high temperatures these barriers would be both large and occurring at small values of r. Therefore, many trajectories would fail to surmount them, and the time a successful trajectory spent inside the associated centrifugal barrier would be relatively short, leading to a slower recombination rate constant and thus to a greater negative temperature dependence of the rate constant.

For the present reaction, the rate constant is about two to three orders of magnitude larger than expected for atom–atom recombinations. It is clear from the foregoing that this is due to the unusually large impact parameters which will lead to successful reaction, ($b < 17.3$ Å), to the slow variation with r of the Coulombic potential surface, and to the consequent lack of centrifugal barriers on the effective potential surface. Although the probability of an adiabatic reaction along surface II–I is slight, once a charge transfer has occurred between the two colliding atoms the resulting ions are trapped on the ionic surface for probably many vibrational periods (unless they have a collision energy greater than the difference between the ionisation energy of Cs and the electron affinity of iodine, when collisional ionisation will result).

THE FALL-OFF REGION

We have already noted that Luther *et al.*[11] reported that at pressures of *ca.* 1–10 atm† the rate of unimolecular decomposition of CsI exhibited an order of *ca.* 0.3 with respect to the bath-gas pressure, which is presumably reflected in the order of the recombination rate constant at these pressures. On the other hand, at pressures of the third body below *ca.* 0.15 atm in the present measurements, we have observed clear third-order behaviour of the recombination reaction. There is thus a remarkably rapid fall-off from third-order to second-order recombination reaction with pressure of the bath gas over a small pressure range. In order to interpret this behaviour,

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† 1 atm = 101 325 Pa.

we consider the expression for the recombination rate at the limit of low pressure given in eqn (xii). We have calculated $k_{\mathrm{rec},0}$ and set $k_7 = \beta_c Z$. k_6 can be estimated from the following expression in terms of the adiabatic reaction probability, $P(E, b)$:

$$k_6 = \int_0^\infty \int_0^{b_{\max}} 2P(E, b) 2\pi b (2E/\mu)^{1/2} f(E)\, \mathrm{d}b \mathrm{d}E$$
$$= 2\pi b_{\max}^2 \pi^2 (\Delta E_p{}^2 R_x 2)/(he^2). \qquad \text{(xxiii)}$$

k_{-6} can therefore be estimated to be $8.6 \times 10^8\ \mathrm{s}^{-1}$. Such a low value for k_{-6} may be understood if we write

$$k_{-6} \approx 2\nu(E_{0A})\bar{\mathrm{P}}. \qquad \text{(xxiv)}$$

Here $\bar{P}$ is the thermally averaged probability of the ionic CsI* complex dissociating adiabatically to atoms, and $\nu(E_{0A})$ is the vibrational frequency in the Coulombic well of energy levels slightly greater than E_{0A}. This frequency can be estimated by calculating the lifetime of one vibrational period of the CsI* complex from eqn (xviii):

$$\tau(E) = (2\mu)^{1/2} b_{\max}{}^{-2} \int_0^{b_{\max}} \mathrm{b}2 \int_{r_{\min}}^{r_{\max}} [E(1 - b^2/r^2) - V]^{-1/2}\, \mathrm{d}r\, \mathrm{d}b \qquad \text{(xxv)}$$

where $r_{\max}$ is now the turning point on the outer branch of the Coulombic well. This method indicates that $\nu(E_{0A}) \approx 3 \times 10^{11}\ \mathrm{s}^{-1}$. Substitution of this value into eqn (xxiv), together with a value of $2\bar{P} = 0.0031$, indicates that $k_{-6} = 9.3 \times 10^8\ \mathrm{s}^{-1}$. This is in good agreement with the estimate of k_{-6} made from the rate data (see above). This low value of k_{-6} emphasises quantitatively how trajectories will be trapped on the ionic diabatic surface I-III once formation of the ionic complex has occurred.

It will also now be apparent that this small value of k_{-6} is the cause of the rapid fall-off from third to second order of the recombination rate constant. Examining the expression for k_{rec} as a function of [M], *i.e.* reaction (6), it will be seen that the order of the reaction with respect to [M] is governed by the relative size of k_{-6} and k_7[M]. In fact, these become equal at $T = 491$ K when $[\mathrm{M}] = 9.9 = 10^{19}\ \mathrm{cm}^{-3}$, or only 0.65 atm. In order to interpret fully our results at low pressures of M and to compare them with the high-temperature recombination rate constant derived from the shock-tube data[6] at high pressure,[11] we have carried out a detailed calculation of k_{rec}:

$$k_{\mathrm{rec}} = \int_0^\infty \int_0^{b_{\max}} \frac{k_6(E, b) k_7[\mathrm{M}]\, \mathrm{d}b\, \mathrm{d}E}{k_{-6}(E, b) + k_7[\mathrm{M}]}. \qquad \text{(xxvi)}$$

$k_{-6}(E)$ is given by eqn (xxv) multiplied by a probability factor ($2P$), and k_6 is given by eqn (xx) multiplied by the same probability factor. The resulting plots of k_{rec} against [M] at $T = 491$ and 2400 K are illustrated in fig. 7. On the low-temperature plot the data from the present work are described well by the calculation, and that there is a slight degree of curvature over the pressure range that we were able to study using the present system. We therefore prefer the value of

$$k_{\mathrm{rec},0}(T = 491\ \mathrm{K}) = 9.1 \times 10^{-31}\ \mathrm{cm}^6\ \mathrm{atom}^{-2}\ \mathrm{s}^{-1}$$

which modifies our experimental measurement of $k_{\mathrm{rec},0}$ by including the calculated effects of a fall-off over the pressure range employed in these measurements. (We

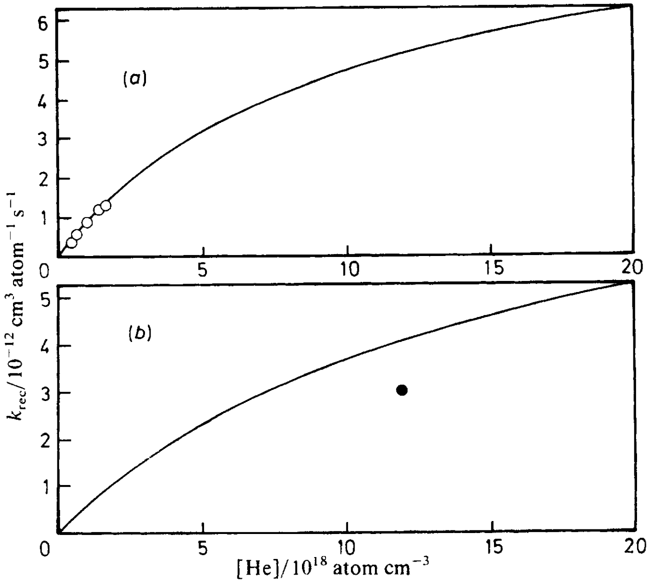

Fig. 7. Plots of the calculated second-order rate coefficients (k_{rec}) for the reaction between Cs + I + He as a function of the concentration of helium based on the Lindemann energy transfer mechanism modified to take account of the probability of adiabatic collisions between Ca and I atoms. (*a*) $T = 491$ K (○, this work); (*b*) $T = 2400$ K (●, shock-tube data, Tröe and coworkers).

assume here an error of *ca.* 25% to take account of approximations and assumptions in the calculation.)

The temperature dependence of $k_{rec,0}$ can be expressed as

$$k_{rec,0}(491 < T/\mathrm{K} < 2400) = 4.1 \times 10^{-30} T^{-0.24}.$$

On the plot of k_{rec} against [M] at $T = 2400$ K we include the datum-point derived from the shock-tube study.[11] Considering the experimental and theoretical approximations involved, there is a good agreement between calculation and experiment. More important, the order of the reaction is very well accounted for. If we express $k_{rec} \propto [\mathrm{M}]^{\alpha}$, then α varies from 0.54 at $[\mathrm{M}] = 1.2 \times 10^{19}$ cm^{-3}, at which the rate constant was measured, to 0.23 at $[\mathrm{M}] = 4.8 \times 10^{19}$ cm^{-3}, the maximum pressure achieved in the shock-tube work.[11] These values of α straddle the rough value of 0.3 found in the shock-tube experiments.

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[1] M. J. Howard and I. W. M. Smith, *Progr. React. Kinet.* 1983, **12**, 55.
[2] D. Husain, J. M. C. Plane and Chen Cong Xiang, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 1465.
[3] D. Husain, J. M. C. Plane and Chen Cong Xiang, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 1619.
[4] D. Husain, J. M. C. Plane and Chen Cong Xiang, *J. Chem. Soc., Faraday Trans. 2*, 1985, **81**, 561.
[5] D. Husain, J. M. C. Plane and Chen Cong Xiang, *J. Chem. Soc., Faraday Trans. 2*, 1985, **81**, 769.
[6] A. M. C. Moutinho, J. A. Aten and J. Los. *Physica (Utrecht)*, 1971, **53**, 471.
[7] J. Los and A. W. Kleyn, in *Alkali Halide Vapours*, ed. P. Davidovits and D. L. McFadden (Academic Press, New York, 1979).
[8] R. B. Bernstein, *Chemical Dynamics* via *Molecular Beam and Laser Techniques* (Clarendon Press, Oxford, 1982).
[9] M. B. Faist and R. D. Levine, *J. Chem. Phys.*, 1976, **64**, 2953.
[10] A. P. M. Baede, *Adv. Chem. Phys.*, 1975, **30**, 463.
[11] K. Luther, J. Tröe and H. Gg. Wagner, *Ber. Bunsenges. Phys. Chem.*, 1972, **76**, 53.
[12] D. Husain, J. M. C. Plane and Chen Cong Xiang, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 713.
[13] C. R. Vidal and J. Cooper, *J. Appl. Phys.*, 1969, **40**, 3370.
[14] *J.A.N.A.F. Thermochemical Tables, J. Phys. Chem. Ref. Data Suppl.*, 1974, **3**, 311.
[15] P. Davidovits and D. C. Brodhead, *J. Chem. Phys.*, 1967, **46**, 2968.
[16] G. E. Gogin and G. E. Kimball, *J. Chem. Phys.*, 1948, **16**, 1035.
[17] *C.R.C. Handbook of Bimolecular and Termolecular Reactions*, J. A. Kerr and S. J. Moss (C.R.C. Press Inc., Boca Raton, Florida, 1981), vol. I.
[18] *Atomic Energy Levels, Natl Bur. Stand. (U.S.) Circ. 467*, (U.S. Department of Commerce, Washington D.C., 1958), vol. I-III.
[19] D. Husain and R. J. Donovan, *Adv. Photochem.*, (Wiley-Interscience, New York, 1971), vol. 8, p. 1.
[20] R. J. Donovan and D. Husain, *Trans. Faraday Soc.*, 1966, **62**, 11.
[21] R. J. Donovan and D. Husain, *Nature (London)*, 1966, **209**, 609.
[22] J. J. Deakin and D. Husain, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 41.
[23] J. J. Deakin and D. Husain, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 1063.
[24] G. Liuti and J. E. Mentall, *Rev. Sci. Instrum.*, 1968, **39**, 1767.
[25] R. J. Donovan, F. G. M. Hathorn and D. Husain, *Trans. Faraday Soc.*, 1968, **64**, 1228.
[26] F. G. M. Hathorn and D. Husain, *Trans. Faraday Soc.*, 1969, **65**, 2687.
[27] J. J. Deakin, D. Husain and J. R. Wiesenfeld, *Chem. Phys. Lett.*, 1971, **10**, 146.
[28] M. J. D. Powell, personal communication quoted in D. Husain and N. K. H. Slater, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 606.
[29] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, London, 1934).
[30] M. W. Zemansky, *Phys. Rev.*, 1929, **34**, 213.
[31] E. W. Abrahamson, L. J. Andrews, D. Husain and J. R. Wiesenfeld, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 48.
[32] M. Polyanyi, *Atomic Reactions* (Williams and Norgate, London, 1932).
[33] W. S. Struve, J. R. Krenos, D. L. McFadden and D. R. Herschbach, *J. Chem. Phys.*, 1975, **62**, 404.
[34] J. K. K. Ip and G. Burns, *J. Chem. Phys.*, 1972, **56**, 3155.
[35] H. van den Burgh, N. Benoit-Guyot and J. Tröe, *Int. J. Chem. Kinet.*, 1977, **9**, 223.
[36] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
[37] *Alkali Metal Halide Vapours*, ed. P. Davidovits and D. L. McFadden, (Academic Press, New York, 1979).
[38] E. S. Rittner, *J. Chem. Phys.*, 1951, **19**, 1030.
[39] P. W. Fowler and N. C. Pyper, *Proc. R. Soc. London, Ser. A*, 1985, **398**, 377.
[40] M. Karplus and R. N. Porter, *Atoms and Molecules* (W. A. Benjamin, Menlo Park, 1970), p. 260.
[41] T. M. Miller and B. Bederson, Adv. Atom. Mol. Phys., 1977, **3**, 1.
[42] R. Grice and D. R. Herschbach, Mol. Phys., (1974), **27**, 159.
[43] C. Zener, *Proc. R. Soc. London, Ser. A*, 1933, **140**, 660.
[44] R. Hartig, H. A. Olschewski, J. Tröe and H. Gg. Wagner, *Ber. Bunsenges. Phys. Chem.*, 1968, **72**, 1016.
[45] D. L. Bunker, *J. Chem. Phys.*, 1960, **32**, 1001.
[46] J. Tröe, *J. Chem. Phys.*, 1977, **66**, 4745; 4758.
[47] D. L. Bunker, *Theories of Elementary Gas Reactions* (Pergamon, Oxford, 1966).
[48] I. W. M. Smith, *Int. J. Chem. Kinet.*, 1984, **16**, 423.
[49] G. J. Janz, R. P. T. Topkins, C. B. Allen, J. R. Downey Jr and S. K. Singer, *J. Phys. Chem. Ref. Data Ser.*, 1977, **6**, 409.
[50] *C.R.C. Handbook of Chemistry and Physics*, ed. R. C. Weast (C.R.C. Press Inc., Boca Raton, Florida, 1983 64th edn).

[51] H. Endo, G. Glanzer and J. Tröe, *J. Phys. Chem.*, 1975, **83**, 2083.
[52] S. H. Luu and J. Tröe, *Ber. Bunsenges. Phys. Chem.*, 1975, **77**, 325.
[53] M. Heymann, H. Hippler and J. Tröe, *J. Chem. Phys.*, 1984, **80**, 1853.

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