GENERAL DISCUSSION

Prof. F. S. Rowland (*University of California, Irvine*) said: Steinfeld's motion picture of the trajectories of $I+I_2$ reactions showed several cases of " multiple-collision " trajectories. What was the typical time-scale for the existence in close proximity of one another of all three iodine atoms " ?

Prof. J. I. Steinfeld (*M.I.T., Cambridge, Mass.*) said: Durations of the fifty-four $I+I_2$ trajectories which we calculated ranged from a low limit of 1.6×10^{-12} s to a high one of 1.11×10^{-11} s, with an average duration of 3.58×10^{-12} s. All the collinear trajectories had a near-minimum duration, independent of the phase of the oscillator in the collision, while nearly all the non-collinear trajectories lasted for two or three vibrations of the I_3 complex.

Prof. J. Troe (*Lausanne*) said: I would mention two consequences of the large effective cross-section of vibrationally excited I_2 molecules demonstrated by Steinfeld. First, the thermal decomposition of I_2 undergoes a transition from a second-order reaction to a first-order reaction at carrier gas pressures as low as about 30 atm.[1] Here, the slow separation of I atoms becomes the rate-determining step of the dissociation. Secondly, the thermal recombination of two I atoms at room temperature is a third-order reaction only at pressures $\leqslant 0.3$ atm. At 1 atm in Ar, the reaction order is about 2.5. Because the reaction order becomes again 3 at pressures above 3 atm, we attribute this behaviour to the decay of the energy-transfer component of the total recombination mechanism. This should be due to the transition into the range where, for this component, the slow approach of two I atoms becomes rate determining. At pressures above 3 atm, the reaction is again third order and it becomes a pure second-order reaction at pressures in the range 100-1000 atm.[2] We attribute this to the complex component of the recombination mechanism. For this component the transition pressure from third to second order is related to the equilibrium constant for, e.g., the $I+Ar\leftrightharpoons IAr$ complex, and the I—Ar potential parameters may be derived. We used this method systematically for determining a series of different I-carrier gas potential parameters.[2]

Dr. R. F. Heidner (*University of California, Los Angeles*) said: In the spirit of Steinfeld's comparison of experimental data with trajectory calculations for the system $I(^2P)+I_2(B^3\Pi_{0_u^+})$, I would present experimental data [3] for an electronically-adiabatic three-atom process occurring on a repulsive potential surface, viz.,

$$H(^2S)+H_2(X^1\Sigma_g^+, v''=1)\xrightarrow{k_1}H_2(X^1\Sigma_g^+, v''=0)+H(^2S). \tag{1}$$

Our experimental technique combines the use of quantitative vacuum ultra-violet absorption spectroscopy (for H_2) and isothermal calorimetry (for H). The data show that $k_1 = 1.8\pm0.9\times10^8$ l. mol^{-1} s^{-1}, which is approximately 10^3 times faster than the exchange reaction of $H(^2S)$ with $H_2(X^1\Sigma_g^+, v''=0)$.[4] For this system,

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[1] J. Troe and H. Gg. Wagner, *Z. phys. Chem., Frankfurt*, 1967, **55**, 326.
[2] H. Hippler, K. Luther and J. Troe, to be published.
[3] R. F. Heidner III and J. V. V. Kasper, *Chem. Phys. Letters* in press.
[4] W. Schultz and D. J. LeRoy, *J. Chem. Phys.*, 1965, **42**, 3869.

three-dimensional trajectory calculations [1] show that reactive-scattering dominates k_1, in other words, relaxation of $H_2(v'' = 1)$ without atomic exchange is negligible. This study conflicts with a recent quantum-mechanical calculation [2] in one dimension which shows the reactive and non-reactive components of k_1 to be approximately equal. Assuming the three-dimensional trajectory calculations are correct regarding reactive against non-reactive collisions, table 1 compares the experimental and theoretical values for k_1. One concludes from the general agreement of these results that atomic exchange can provide a fast channel for vibrational relaxation even on a totally repulsive potential surface.

TABLE 1.—SUMMARY OF RATE CONSTANT DATA

	$k_R^{1\to 0}$ [a, b]	$k_R^{0\to 0}$ [a, b]	$(k_R^{1\to 0}/k_R^{0\to 0})$
experimental	$1.8 \pm 0.9 \times 10^8$ [c]	1.18×10^5 [d]	$1.5 \pm 0.7_6 \times 10^3$
trajectory	$1.8_3 \times 10^8$ [e, f]	2.53×10^5 [f]	$0.7_2 \times 10^3$
one-dimension	(2.6×10^3) [g]	(5.87) [g]	$0.45 \pm 0.08 \times 10^3$

[a] Units of l. mol^{-1} s^{-1}; [b] subscripts R and N refer to reactive and non-reactive encounters; superscripts reflect the initial and final H_2 vibrational state; [c] based on $k_N^{1\to 0} \approx 0$; [d] $k_R^{0\to 0}$ taken from ref. (2); [e] based on $k_R^{1\to 0} \approx k_R^{1\to 1}$; [f] based on reactant H_2 having $J'' = 0$ only; [g] units of cm^3 molecule^{-1} s^{-1}.

Dr. I. W. M. Smith (*University of Cambridge*) said: Dr. P. M. Wood and I have nearly completed some three-dimensional, classical, trajectory calculations which are designed to explore the possibility that atom-exchange reactions of the type $A+BC \rightarrow AB+C$ can cause efficient vibrational relaxation even where the activation energy for the reaction is appreciable. Model systems, corresponding to the collision partners $H+H_2$ (v = 1 and 2), $H+ClH$ (v = 1 and 2) and $Cl+HCl$ (v = 1 and 2) have been studied. Our rate coefficient for

$$H(^2S)+H_2(X^1\Sigma_g^+, v = 1, J = 2) \rightarrow H_2(X^1\Sigma_g^+, v = 0)+H(^2S)$$

(averaging over J states has not been carried out) is approximately 1.4×10^8 l. mol^{-1} s^{-1}. On equivalent energy hypersurfaces, the various mass combinations give rise to significantly different results. As anticipated by Ridley and Smith,[3] the light mass of the transferable atom in $Cl+HCl$ collisions allows reagent vibrational energy to be efficiently used in overcoming the activation barrier.

In distinguishing which collisions can cause significant vibrational relaxation it is useful to distinguish *three*, rather than two, types: (*a*) those in which reaction to $AB+C$ (or $AC+B$) takes place; (*b*) those in which at some point in the trajectory the A–B (or A–C, if B and C are equivalent) distance becomes less than that between B and C, but the atoms eventually separate to A and BC; (*c*) those in which the B–C distance is always the smallest. We find that type (*c*) collisions are highly vibrationally adiabatic but that (*a*) and (*b*) show similar, and generally large, degrees of inelasticity. In classic collinear collisions, only type (*c*) collisions occur below a well-defined threshold energy and—at least for vibrationally excited molecules—types (*a*) and (*b*) occur almost exclusively above threshold. As a result, even in classical collinear calculations, there is a large probability of energy transfer in non-reactive

[1] M. Karplus and I. Wang, private communication (1971).

[2] (*a*) D. G. Truhlar and A. Kuppermann, *J. Chem. Phys.* 1972, **56**, 2232.
(*b*) A. Kuppermann, private communication (1971).

[3] B. A. Ridley and I. W. M. Smith, *Chem. Phys. Letters*, 1971, **9**, 457.

(i.e., type (*b*)) collisions. In three dimensions, however, the great majority of non-reactive collisions above threshold are of type (*c*) and are elastic. We believe that this—rather than the different dynamics assumed—may cause the apparent discrepancy between the quantum-mechanical (and one-dimensional) calculations and the classical (but three-dimensional) calculations which has been noted by Heidner.

Dr. P. Cadman (*University College of Wales, Aberystwyth*) said: I have some results which support the mechanism of excitation of the $I(^2P_{\frac{1}{2}})$ atoms proposed by Thrush. An investigation of the proportion of $I(^2P_{\frac{1}{2}})$ atoms produced in various reaction led me to react oxygen atoms, produced by a microwave discharge in oxygen, with hydrogen iodide:

$$O+HI \rightarrow OH+I(^2P_{\frac{1}{2}}) \quad (1)$$

$$\rightarrow OH+I(^2P_{\frac{3}{2}}). \quad (2)$$

An intense infra-red emission from the $I(^2P_{\frac{1}{2}})$ atoms was observed and the apparent ratio $k_1/(k_1+k_2)$ was calculated to be about 0.8. In order to explain the much larger fraction of $I(^2P_{\frac{1}{2}})$ atoms produced in this reaction compared to (3)-(4),

$$H+HI \rightarrow H_2+I^*(^2P_{\frac{1}{2}}) \quad (3)$$

$$\rightarrow H_2+I(^2P_{\frac{3}{2}}) \quad (4)$$

it was thought that $O_2(^1\Delta_g)$ which is present in discharged oxygen in relatively large concentrations might be responsible for this high yield. Thrush's results confirm this.

Dr. I. W. M. Smith (*University of Cambridge*) said: Some experiments carried out by Dr. B. A. Ridley and myself confirm Cadman's conclusions. We observed the infra-red chemiluminescence which was emitted when HI was added to (*a*) the products of a microwave discharge through a dilute mixture of O_2(~1 %) in Ar, and (*b*) oxygen atoms generated in the titration reaction $N+NO \rightarrow N_2+O$. In the latter experiments, where metastable molecules of O_2 were excluded, the $I(^2P_{\frac{1}{2}}-{}^2P_{\frac{3}{2}})$ emission at 1.315 μm was greatly reduced. The reaction, $O+HI \rightarrow OH+I$, was also shown to be inefficient at producing vibrationally excited OH, which is consistent with the surprisingly slow rates found for the reactions of oxygen atoms with hydrogen halides.[1]

Dr. M. A. A. Clyne, Dr. J. A. Coxon and **Mr. L. W. Townsend** (*Queen Mary College, London*) said: We wish to report the observation of the $^3\Pi(0^+)$ states of BrF and IF, analogous to I_2 [2] and Br_2,[3] in systems containing singlet oxygen $O_2(^1\Delta_g, {}^1\Sigma_g^+)$, with ground state $^2P_{\frac{3}{2}}$ F, and Br or I atoms. These low-lying $^3\Pi(0^+)$ states correlate with a ground state $^2P_{\frac{3}{2}}$ and a *J*-excited $^2P_{\frac{1}{2}}$ atom. Dissociation to two ground-state atoms can only occur via a potential barrier by curve crossing with 0^+ repulsive states. $Br^2P_{\frac{3}{2}}$ atoms were produced by a microwave discharge in Br_2+Ar mixtures, or by the reaction of Br_2 with the products of a discharge in O_2. $I^2P_{\frac{3}{2}}$ atoms were generated by reaction of ICl with the products of a discharge in O_2. F atoms were generated by a discharge in CF_4+Ar mixtures.

Excitation of XF $^3\Pi(0^+)$ [X = Br, I] may occur, (I) by energy transfer from $O_2\ {}^1\Delta_g$ to X $^2P_{\frac{3}{2}}$, forming X $^2P_{\frac{1}{2}}$, followed by combination of X $^2P_{\frac{1}{2}}$+F $^2P_{\frac{3}{2}}$,

$$X\ {}^2P_{\frac{3}{2}}+O_2\ {}^1\Delta_g, {}^1\Sigma_g^+ \rightarrow X\ {}^2P_{\frac{1}{2}}+O_2X\ {}^3\Sigma_g^-, \quad (1a)$$

$$X\ {}^2P_{\frac{1}{2}}+F\ {}^2P_{\frac{3}{2}}(+M) \rightarrow XF\ {}^3\Pi(0^+)(+M). \quad (1b)$$

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[1] C. Morley, *Ph.D. Thesis*, (University of Cambridge, 1971).

[2] R. G. Derwent, D. R. Kearns and B. A. Thrush, *Chem. Phys. Letters*, 1970, **6**, 115.

[3] M. A. A. Clyne, J. A. Coxon and H. W. Cruse, *Chem. Phys. Letters*, 1970, **6**, 57.

Alternatively, (II), excitation of XF $^3\Pi(0^+)$ may occur by recombination of X $^2P_{\frac{3}{2}}$ + F $^2P_{\frac{3}{2}}$ ground-state atoms, to give XF $^3\Pi(1)$, followed by excitation of $^3\Pi(1)$ to $^3\Pi(0^+)$ by collision with O_2 $^1\Delta_g$, $^1\Sigma_g^+$:

$$\text{X}\ ^2P_{\frac{3}{2}}+\text{F}\ ^2P_{\frac{3}{2}}(+\text{M})\rightarrow\text{XF}\ ^3\Pi(1)(+\text{M});$$

$$\text{XF}\ ^3\Pi(1)+\text{O}_2\ ^1\Delta_g,\ ^1\Sigma_g^+\rightarrow\text{XF}\ ^3\Pi(0^+)+\text{O}_2\text{X}\ ^3\Sigma_g^-.$$

Reaction (1*a*), which has been demonstrated for excitation of I $^2P_{\frac{3}{2}}$ atoms where the energy transfer step is nearly resonant,[1] would involve, for Br $^2P_{\frac{3}{2}}$, a considerable energy discrepancy.

The emission spectra, $^3\Pi(0^+)-\text{X}\ ^1\Sigma^+$, of BrF and of IF, excited by singlet oxygen, appear as intense yellow (BrF) and green (IF) chemiluminescences of appreciable duration. Both spectra (at 1 Torr total pressure) show extensive band systems, virtually all the bands of which, other than the O_2 $b\ ^1\Sigma_g^+-\text{X}\ ^3\Sigma_g^-$ bands, are assigned to the $^3\Pi(0^+)-\text{X}\ ^1\Sigma^+$ transitions of BrF and IF.

Dr. B. A. Thrush (*University of Cambridge*) said: There is good evidence that the process

$$\text{I}(^2P_{\frac{3}{2}})+\text{I}(^2P_{\frac{1}{2}})+\text{M} = \text{I}_2(B^3\Pi_{o^+u})+\text{M} \qquad (1)$$

does not make any significant contribution to the I_2 emission observed in Derwent's experiments.[2] The intensity of such emission would be proportional to the square of the amount of added iodine, since under our conditions the concentrations of both $\text{I}(^2P_{\frac{3}{2}})$ and $\text{I}(^2P_{\frac{1}{2}})$ are strictly proportional to the amount of iodine added. The intensity of I_2 emission is proportional to the amount of iodine added, and to slightly more than the inverse square of the pressure; it is also stronger near the walls at which iodine atoms recombine rapidly. These observations all argue against any significant contribution by reaction (1).

The excitation of $\text{I}_2(A^3\Pi_{1u})$ to $\text{I}_2(B^3\Pi_{o^+u})$ which is faster than one collision in ten is " non-resonant " in the sense that on the average 55 % of the energy of $\text{O}_2(^1\Delta)$ appears as electronic and vibrational energy of the I_2. There is therefore no reason why this molecular excitation process should not be general with both homo- and heteronuclear halogens.

Prof. T. Carrington (*York University, Canada*) (*communicated*): It is pointed out by Derwent and Thrush that their reaction (1) is nearly resonant. This statement can be amplified as follows. When the potential curve for $\text{O}_2(^2\Sigma_g^-)$ is raised by the excitation energy of $\text{I}(^2P_{\frac{1}{2}})$, 0.943 eV, it nearly coincides with the curve for $\text{O}_2(^1\Delta_g)$ over a range of internuclear distance of 0.1 Å on either side of the minimum. Hence the reaction is nearly resonant over a substantial range of internuclear distance. Within the accuracy of Gilmore's plots, the shifted ground-state curve appears to cross the $a(^1\Delta_g)$ curve near the minimum. This indicates an asymptotic intersection of IO_2 surfaces as I recedes from O_2.

Dr. J. F. Ogilvie (*Memorial University of Newfoundland, Canada*) said: To what extent are assumptions or deductions concerning crossing between potential curves (or between the electronic states to which they pertain) dependent on the accuracy with which potential energy functions and vibrational wavefunctions are known for the vibronic states involved?

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[1] R. G. Derwent and B. A. Thrush, this Discussion.

[2] R. G. Derwent and B. A. Thrush, *J.C.S. Faraday II*, 1972, **68**, 720.