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# Quenching of $I^*({}^2P_{1/2})$ by Atomic and Molecular Hydrogen and Halogens

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A new experimental method has been devised by which it is possible to study the deactivation of  $I^*(5\,^2P_{1/2})$  by radical atoms as well as by stable molecular species. A small, steady-state concentration of I atoms is generated in a discharge-flow system, and then a fraction of these atoms is directly excited using the output from a pulsed iodine-atom, photochemical laser. The subsequent decay of  $I^*(5\,^2P_{1/2})$  is observed by monitoring the  $I_2(B \rightarrow X)$  emission, the  $B[{}^{3}\Pi(0_{u}^{+})]$  state of  $I_2$  being formed by recombination,  $I^*+I+M \rightarrow I_2(B)+M$ . The following quenching rate constants (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) at room temperature have been determined:  $k_{H_2} = (1.03 \pm 0.06) \times 10^{-13}$ ,  $k_{B_T} = (5.5 \pm 0.1) \times 10^{-11}$ ,  $k_{Cl_2} \le 5 \times 10^{-14}$ ,  $k_H = (4 \pm 2) \times 10^{-14}$ ,  $k_I \le 5 \times 10^{-13}$ ,  $k_{B_T} = (5.1 \pm 1.9) \times 10^{-13}$  and  $k_{Cl} = (2 \pm 1) \times 10^{-11}$ .

The rates of quenching of iodine atoms in their  $(5^2 P_{1/2})$  state have now been measured for 20 years.<sup>1</sup> As well as fundamental interest in the dynamics of such electronically non-adiabatic processes, such studies have been stimulated by the discovery<sup>2</sup> and subsequent development<sup>3</sup> of the pulsed photochemical iodine-atom laser oscillating on the magnetic dipole transition between the two spin-orbit components of the ground electronic term:  $I^*(5^2P_{1/2}) \rightarrow I(5^2P_{3/2})$ . More recently, interest in the kinetics of  $I^*(5^2 P_{1/2})$  atoms (which will be referred to from hereon as I\*) has revived as a result of research on the continuous-wave, chemically pumped oxygen iodine laser.<sup>4</sup> Although the detailed mechanism of this device is not yet fully established, it has become clear that its successful operation brings into question<sup>5-7</sup> some of the laboratory measurements made on  $I^*$  quenching rates. Although rate data on the quenching of  $I^*$  atoms are available for an extensive range of collision partners, there remains one serious omission: namely, the absence of measurements on quenching by free radicals. Such processes involving two atoms are especially interesting from a theoretical point of view,<sup>8</sup> since they constitute the simplest case of a non-adiabatic collisional process. Furthermore, the potential curves between which the non-radiative transition must occur may be known (or might in the future be characterised) from spectroscopic measurements or *ab initio* calculations.

Unfortunately, the experimental methods that have been used to measure the rates of quenching of I\* by stable collision partners cannot generally be used, even in a modified form, when the quencher is a reactive radical. Virtually all previous measurements have relied upon the generation of I\* atoms by flash photolysis or pulsed laser photolysis of a suitable precursor, usually an alkyl or perfluoroalkyl iodide. However, such species react rapidly with, for example, H, Cl or Br atoms. As a result it has been necessary to develop a new technique for studying I\* quenching by these species.

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In the experiments which we report in the present paper, iodine atoms are created in a discharge-flow system, along with an excess of a second atomic radical. A fraction of the I atoms is then directly excited to the  $(5^2 P_{1/2})$  state by irradiation with the pulsed output from a photochemical iodine-atom laser. The subsequent decay of the I\* concentration is monitored by observing the time-resolved emission intensity associated with the formation of I<sub>2</sub> molecules in the  $B^{3}\Pi(0_{\mu}^{+})$  state:<sup>1,9</sup> *i.e.* 

$$\mathbf{I}^* + \mathbf{I} + \mathbf{M} \rightarrow \mathbf{I}_2[B^{3}\Pi(\mathbf{0}_u^+)] + \mathbf{M}$$
(1a)

$$I_2[B^{3}\Pi(0_u^+)] \rightarrow I_2(X^{1}\Sigma_g^+) + h\nu$$
(1b)

This general experimental method, in which pulsed excitation and real-time measurement are combined with discharge-flow techniques to generate steady-state concentrations of unstable species, has been used by a number of research groups to determine relaxation rates of vibrationally excited molecules by radical atoms.<sup>10</sup> In its present form the technique has been checked by measuring rates of deactivation of I\* by  $H_2^{11-20}$  and  $Br_2^{21-25}$  processes for which the rate constants at room temperature appear to be well established. Then the method has been applied to measure the rates of I\* quenching by atomic hydrogen and atomic bromine. In addition, we report preliminary measurements for the quenching of I\* by  $Cl_2$  and Cl, and an upper limit for the rate constant for quenching of I\* by  $I_2$ .

## **EXPERIMENTAL**

### SUMMARY OF THE METHOD

The experiments were performed in a discharge-flow apparatus which was a modification of that used by Howard and Smith to measure the rates of the radical-radical reactions between OH and N,<sup>26</sup> O<sup>26</sup> and D<sup>27</sup> atoms. In all our experiments, the preparation of atomic radicals was based on the primary production of atomic hydrogen. All these atoms, or some proportion of them, could be converted into I atoms *via* the fast reaction  $(k_2 = 2.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K})^{28}$ 

$$H + HI \rightarrow H_2 + I. \tag{2}$$

Br or Cl atoms were generated by adding Br<sub>2</sub>, HBr or Cl<sub>2</sub> to react with the excess of H atoms.

A fraction of the steady-state concentration of ground-state iodine atoms could be excited to the  $5^2 P_{1/2}$  state using the output from a pulsed photochemical iodine-atom laser. The  $I_2(B \rightarrow X)$  chemiluminescence resulting from processes (1*a*) and (1*b*) was used to observe the decay of the I\* concentration following the laser pulse. Signals generated by a single laser shot were quite adequate for analysis.

### THE DISCHARGE-FLOW AND GAS-HANDLING SYSTEMS

The main gas stream comprised hydrogen diluted in argon and flowed through the cavity of a 2450 MHz microwave discharge unit (Electromedical Supplies, Microtron 200 Mk 3). these gases were taken direct from cylinders (Air Products: purity of Ar>99.998%; purity of H<sub>2</sub>>99.97%) and entered the apparatus through silicone oil 'bubblers'. Their flows were controlled by needle valves and measured using rotameters accurate to  $\pm 2\%$  (MeTeRaTe, Glass Precision Engineering).

The flow and hence the steady-state concentration of atomic hydrogen could be established by titration with NO<sub>2</sub> using the HNO<sup>\*</sup> emission as indicator.<sup>29</sup> NO<sub>2</sub> could be added through injectors upstream, downstream or in the centre of the reaction cell. The analysis of these titrations closely followed that described by Howard<sup>26-27,30</sup> and is discussed in more detail elsewhere.<sup>31</sup> For the experiments on quenching by H atoms, the Pyrex cell (*ca.* 40 cm in length and of 35 mm internal diameter) was washed in HF and left uncoated. Titrations with  $NO_2$  indicated *ca.* 40% loss of H atoms by heterogeneous recombination during passage through the main cell, and this was allowed for in estimating concentrations of H. For measurements with the halogens, the walls of the main cell were coated with halogenocarbon wax<sup>32</sup> (Vanderbilt Export Corp., type 15-00) to minimise wall recombination of halogen atoms.

The degree of dissociation of  $H_2$  varied between 10 and 60%. It depends on the power coupled to the discharge, the coating on the quartz tube passing through the cavity, and the composition, flow rate, total pressure and purity of the gas. In our experiments the discharge tube was coated with boric acid and no special effort was made to purify the gases. The latter would have been counterproductive in many of our experiments since it could have greatly reduced the ratio of atomic to molecular concentrations of hydrogen.

In experiments designed to measure the rates of quenching by molecular species, the flow of hydrogen was small, its fractional dissociation was high, and the H atoms produced (initial concentration *ca.*  $10^{14}$  cm<sup>-3</sup>) were converted entirely into I atoms by addition of a small excess of HI downstream of the discharge and upstream of the main cell. H<sub>2</sub>, Br<sub>2</sub> or Cl<sub>2</sub> was then added directly to the gas flow once all the H atoms had been removed by reaction (2).

Larger H atom concentrations were generated for experiments on quenching by radical atoms. Addition of HI was then used to convert only a proportion of these atoms into I. To study quenching by H atoms, several series of experiments were performed. In each series the  $H_2$  flow and the initial H atom flow were kept constant and the rates of removal of I<sup>\*</sup> atoms were determined as a function of the amount of HI added. As the flow of HI was increased, the H atom concentration fell whilst those of  $H_2$  and I increased. The analysis of these results is described in the next section.

To create Br atoms, HBr or  $Br_2$  were added. These species were converted stoichiometrically to Br atoms by the reactions

$$H + HBr \rightarrow H_2 + Br \tag{3}$$

or

$$H + Br_2 \rightarrow HBr + Br \tag{4}$$

and

$$H + HBr \rightarrow H_2 + Br$$
 (3)

 $(k_3 = 3.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}; k_4 = 5.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K).<sup>33,34</sup> As long as there is an excess of atomic hydrogen present, these reactions will ensure that effectively all the bromine present is atomic bromine. The flow of HBr or Br<sub>2</sub> was added, with a small constant flow of HI through an injector *ca.* 1 cm (2 ms) upstream of the observation zone. The presence of an excess of H atoms could be confirmed by observing the intensity of the Br<sub>2</sub> afterglow associated with recombination of bromine atoms.<sup>35</sup> As long as this emission continued to increase in intensity as more HBr or Br<sub>2</sub> was added, there were H atoms in excess. Within this regime it was unnecessary to know the absolute concentration, [H], since the measured flow of HBr or Br<sub>2</sub> provided the best measure of [Br].

When  $Cl_2$  is added to gas containing an excess of H atoms at concentrations of *ca*.  $10^{15}$  cm<sup>-3</sup>, the reaction

$$H + Cl_2 \rightarrow HCl + Cl \tag{5}$$

 $(k_5 = 1.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{34}$  went to completion in less than the 2 ms which it took gas to flow from the injection point to the observation zone in our experiments. On the other hand, the reaction

$$H + HCl \rightarrow H_2 + Cl \tag{6}$$

is slow  $(k_6 = 4.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{34}$  and would scarcely occur on this timescale. Consequently we assumed that the steady-state concentration of Cl atoms obtained when Cl<sub>2</sub> was added was equal to the initial concentration of Cl<sub>2</sub>, and we estimate that this assumption should be correct within  $\pm 5\%$  for the conditions of our experiments. To avoid

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any complications that might arise from the rapid reaction<sup>34</sup>

$$Cl + HI \rightarrow HCl + I$$
 (7)

the HI was injected ca. 14 ms before the  $Cl_2$  was added, to ensure that reaction (2) was complete. As in the experiments with bromine, the presence of an excess of H atoms could be confirmed by measuring how the Cl<sub>2</sub> afterglow<sup>36</sup> varied as the flow of Cl<sub>2</sub> was varied.

All the experiments that are reported here were carried out at room temperature. The total pressure in the main cell was measured with a capacitance manometer (Furness Controls, model FC0 40) and was always between 4.0 and 4.5 Torr (1 Torr  $\approx$  133 N m<sup>-2</sup>). All gases except argon and hydrogen were stored pure or diluted in argon in storage bulbs. Their flows were controlled with needle valves and determined by observing the rate at which the pressure fell as gas flowed from a calibrated volume. The sources and procedures for purifying the gases were as follows.

Hydrogen iodide was prepared by the reaction of excess tetrahydronaphthalene on  $I_2$ :<sup>37</sup>

$$C_{10}H_{12} + 2I_2 \rightarrow C_{10}H_8 + 4HI$$
 (8)

N2 was bubbled slowly through the reagents which were under reflux. The N2 stream carried the gaseous HI through a trap at 256 K to a liquid- $N_2$  trap where it condensed. This product was purified by degassing at 77 K, low-temperature distillation (195 to 77 K) and finally degassing at 144 K. When not in use, the HI was kept frozen down to prevent decomposition to  $H_2$  and  $I_2$ . Nitrogen dioxide was taken from a cylinder (Matheson 'research' grade; 99.5% pure), evaporated from 13X grade molecular sieve and then degassed at 195 K. In measuring its flow rate, due allowance was made for the  $2NO_2 \rightleftharpoons N_2O_4$  equilibrium. Hydrogen bromide was taken from a cylinder (Matheson 'research' grade; 99.8% pure), degassed at 77 K and then distilled from 195 to 77 K. Bromine (Fisons analytical-reagent grade; 99% pure) was degassed at 77 K and distilled from 273 to 77 K. Chlorine (Matheson 'research' grade; 99.9% pure) was degassed at 77 K and distilled from 195 to 77 K. Perfluoropropyl iodide was used as the source of I\* atoms in the laser (see below). It was obtained from Fluorochem Ltd as a volatile liquid, degassed at 77 K and then distilled from 256 to 77 K.

### THE IODINE-ATOM LASER

The iodine-atom laser was constructed according to a simple, closed-cycle design of the type described by Fuss and Hohla.<sup>38</sup> This allows one to remove  $I_2$  which is formed following flash photolysis of the laser gas, in our case  $n-C_3F_7I$ . The laser can then be fired many times at ca. 1 min intervals before it needs replenishment. This repetition rate was quite adequate for our single-shot experiments.

The laser tube itself was made of quartz. It was 1 m long, with an internal diameter of 10 mm and was fitted at both ends with quartz windows set at Brewster's angle. The flashlamp surrounded this tube in a coaxial configuration and was wrapped with aluminium foil to maximise the irradiation of the gas in the laser tube. The optical cavity was 1.2 m long and consisted of a total, gold-coated, reflector of 4 m radius-of-curvature and a quartz flat which was partially coated in gold to give ca. 10% reflectance. The output beam had a cross-sectional area of ca.  $0.4 \text{ cm}^2$ .

Circulation of the  $C_3F_7I$  was maintained with a simple fan constructed from Pyrex. The laser tube was initially filled to 300 Torr but a condenser in the closed-cycle system was then cooled to -8 °C, at which temperature the vapour pressure of C<sub>3</sub>F<sub>7</sub>I is ca. 100 Torr. In this way the cold trap, as well as removing  $I_2$ , also served to control the pressure of the lasing gas at a suitable value. At -8 °C the vapour pressure of I<sub>2</sub> is 20 mTorr.

The annular space which served as the flashlamp was filled with ca. 10 Torr of krypton. Brass end-pieces served to seal this portion of the assembly and to serve as electrodes. An aluminium tube surrounded the whole assembly and was electrically insulated from the positive electrode, but was in contact with the ground electrode. It served to reduce the

impedance of the circuit and was also very effective in minimising high-frequency interferences which were generated when the flashlamp was fired.

Usually 1125 J (15 kV; 10  $\mu$ F) were dissipated through the flashlamp. The laser pulse energy obtained was *ca.* 100 mJ, as measured by a joulemeter (Gen-Tec, model ED-200). Energies up to 250 mJ could easily be obtained, but were not of any advantage in the present experiments, as they could have introduced complications (see below). Before entering the reaction cell the laser beam passed through a GeAs 'cut-on' filter (transmission for  $\lambda > 0.9 \ \mu$ m). This removed scattered light from the flashlamp, which would have been observed by the photomultiplier used to monitor the I<sub>2</sub>(*B*-*X*) emission. The filter and CaF<sub>2</sub> entrance window to the cell attenuated the laser pulse energy to *ca.* 55 mJ or 9×10<sup>20</sup> photon cm<sup>-2</sup>.

## OBSERVATION OF CHEMILUMINESCENT SIGNALS

The steady-state emissions from HNO<sup>\*</sup>,  $Br_2^*(A \to X)$  and  $Cl_2^*(A \to X)$  were observed to establish the concentrations of H atoms and to confirm that H atoms were in excess during experiments designed to measure the rates of quenching by Br or Cl atoms. These observations were made using a red-sensitive photomultiplier (EMI 9781R or RCA C7164R) downstream from the reaction cell [this is PM2 shown in fig. 1 of ref. 26(b) and (27)]. All these emissions were observed through a Wratten 88A filter, which transmits wavelengths >725 nm.

Time-resolved emission from  $I_2[B^{3}\Pi(0_{u}^{+})]$ , following excitation of iodine atoms to the  $5^{2}P_{1/2}$  state, was observed by a photomultiplier (RCA 1P28) through a Wratten 38A filter. The photomultiplier was located midway along the reaction cell [it is PM1 shown in fig. 1 of ref. 26(b) and (27)].

The intensity of the emission from  $I_2(B^3\Pi(0_u^+)]$  formed in the recombination of  $I^*(5^2P_{1/2}) + I(5^2P_{3/2})$  atoms is proportional to the product of the concentrations of atoms in these states. Since the net rate of atomic recombination is slow relative to the rate of  $I^*$  quenching in our experiments, the total concentration of iodine atoms,  $[I^*]+[I]$ , remains constant. Given exponential decay of the excited-state concentration,

and

$$[I^*] = [I^*]_0 \exp(-k_{1st}t)$$

$$[I] = [I]_0 + [I^*]_0 [1 - \exp(-k_{1st}t)]$$

where  $[I^*]_0$  and  $[I]_0$  are concentrations of excited and ground state atoms immediately following the laser pulse. It is then easy to show that the intensity, I, of the  $I_2(B \rightarrow X)$  emission is proportional to

$$I(B \rightarrow X) \propto \exp(-k_{1st}t) - f_0^* \exp(-2k_{1st}t)$$

where  $f_0^*$  is the fraction of the total concentration of iodine atoms excited by the laser pulse, i.e.  $f_0^* = [I^*]_0/([I]_0 + [I^*]_0)$ . Strictly then, the intensity of the observed emission varies with time as the difference between two exponentials with time constants differing by a factor of two. However, even with the  ${}^2P_{1/2} - {}^2P_{3/2}$  transition saturated so that  $f_0^* = \frac{1}{3}$ , the second term in the expression for  $I(B \rightarrow X)$  would be quite small. In practice it is not easy to determine  $f_0^*$ . So to reduce the number of parameters required to fit the experimental traces we worked at reduced laser energy, in order to keep  $f_0^*$  small, and fitted the recorded traces to a single exponential function starting some time after the peak signal:

$$I(B \rightarrow X) \approx A \exp(-k_{1st}t) + B.$$

The validity of this assumption was checked by fitting some curves several times, starting the fit at different points after the peak signal. The derived values of  $k_{1st}$  showed no systematic variation, and we conclude that the assumption of single-exponential fitting must be valid within the statistical error of the fitting routine (*ca.* 10%).

The signals from the photomultiplier were digitised in a transient recorder (Data laboratories, DL905) and recorded on paper tape. These data were then fitted by a non-linear least-squares routine using the University of Cambridge mainframe computer. The digitised data and the fitted exponential curve could be plotted out. A typical result is shown in fig. 1.

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Fig. 1. Typical trace of time-resolved chemiluminescence of  $I_2(B \rightarrow X)$  following direct excitation of I atoms and subsequent recombination of excited, I<sup>\*</sup>, and ground-state I atoms.

## **RESULTS AND DISCUSSION**

Quenching of  $I^*(5^2 P_{1/2})$  by molecular and atomic hydrogen

Quenching rates of  $I^*(5^2 P_{1/2})$  by  $H_2$  were determined using a small fixed flow of  $H_2$  through the discharge. A slight excess of HI was then added to create I atoms and a larger, variable amount of  $H_2$  was added to alter the quenching rate. The conditions and results for one series of experiments is shown in fig. 2. Combined with the results of a second run with a rather larger I atom concentration  $(1.5 \times 10^{14} \text{ cm}^{-3} \text{ rather than } 5.7 \times 10^{13} \text{ cm}^{-3})$  and smaller  $[H_2]/[I]$ , these data yield a rate constant for quenching by  $H_2$  of  $(1.03 \pm 0.06) \times 10^{-13} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>, where the error limits represent a single standard deviation. As can be seen from table 1, this result is in entirely satisfactory agreement with previous measurements.<sup>11-20</sup>

Optoacoustic experiments by Hunter and Kristjansson<sup>20</sup> have shown that quenching of  $I^*$  by  $H_2$  occurs entirely by near-resonant electronic-to-vibrational energy transfer:

$$I^* + H_2(v=0) = I + H_2(v=2); \qquad \Delta E = 475 \text{ cm}^{-1}$$
 (9)

which has an equilibrium constant of 0.216 at 298 K. In those of our experiments where the concentration of H<sub>2</sub> was not in large excess over that of atomic iodine, one might have expected to see non-exponential decays owing to the establishment of the equilibrium represented by eqn (9). No such effects were detected, suggesting that the removal of H<sub>2</sub>(v = 2) molecules by vibrational-to-vibrational energy exchange with H<sub>2</sub>(v = 0):

$$H_2(v=2) + H_2(v=0) = 2H_2(v=1); \qquad \Delta E = 242 \text{ cm}^{-1}$$
 (10)

was fast enough to prevent significant 'back-transfer' of energy from  $H_2(v=2)$  to I. The calculated value<sup>39</sup> of the rate constant for reaction (10), *i.e.*  $k_{10} = 7.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , would be large enough to account for our observations.

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Fig. 2. First-order decay coefficients plotted against concentration of added  $H_2$ .

k	method <sup>a</sup>	ref.
0.88	FP(HI)/PP	11
4	$FP(CF_{3}I)/RE$	12
$1.3 \pm 0.1$	$FP(CF_3I)/RA$	13, 14
$1.1 \pm 0.1$	$FP(C_2F_5I)/RA$	15
$1.20 \pm 0.14$	$FP(CF_3I)/RA$	16
$0.98\pm0.10$	FP/RA	17
$1.20 \pm 0.03$	FP(CH <sub>3</sub> I)/RA	18
$1.15 \pm 0.07$	$PLP(I_2)/RE$	19
$1.1 \pm 0.3$	$MP(CH_3I, CD_3I)/OA$	20
$1.03\pm0.06$	DLE(I)/CL	present work

**Table 1.** Comparison of rate constants  $(k/10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$  at room temperature for quenching of  $I^*(5\,^2P_{1/2})$  by H<sub>2</sub>

<sup>a</sup> I\* atoms generated by flash photolysis (FP), pulsed laser photolysis (PLP) or modulated photolysis (MP) of the named precursor, or by direct laser excitation (DLE) of I atoms. Decay of I\* atoms observed by plate photometry (PP),  ${}^{2}P_{1/2} \rightarrow {}^{2}P_{3/2}$ resonance emission (RE), resonance absorption (RA), optoacoustic techniques (OA), or  $I_{2}(B \rightarrow X)$  chemiluminescence (CL).

Preliminary measurements on the decay of  $I^*$  atoms in the presence of larger concentrations of discharged hydrogen soon indicated that quenching by atomic hydrogen was relatively slow. In order to measure the rate of this process the following strategy was adopted. Series of experiments were carried out in which a relatively large flow of hydrogen was passed through the microwave discharge. The flow, and therefore the steady-state concentration, of H atoms was established by



Fig. 3. First-order decay coefficients plotted against concentration of HI. The intercepts yield  $k_{1st}^{\circ} = A + k_{H_2}[H_2]_0 + k_{H}[H]_0.$ 

titration with NO<sub>2</sub> and was then kept constant within a given series of experiments. In each experiment of a series, a different flow of HI, less than that of atomic hydrogen, was added to the gas flow. This quantitatively decreased the H atom concentration and correspondingly increased the concentrations of  $H_2$  and I. For each addition of HI,  $k_{1st}$ , the pseudo-first-order constant describing the removal of I<sup>\*</sup>, was determined, and the values of  $k_{1st}$  were then plotted against the concentration of added HI. Plots for a number of different H and  $H_2$  flows are shown in fig. 3. The first-order decay constants in these experiments should be given by

$$k_{1st} = A + k_{H}, ([H_2]_0 + [HI]) + k_{H}([H]_0 - [HI]) + k_{I}[HI]$$

where  $k_{\rm H}$ ,  $k_{\rm H}$  and  $k_{\rm I}$  are the second-order rate constants for collisional quenching of I<sup>\*</sup> by  $H_2$ , H and I, respectively, and A allows for removal by all other processes, such as diffusion and quenching at the walls of the reaction cell.  $[H_2]_0$  and  $[H]_0$ are the concentrations of molecular and atomic hydrogen in the absence of HI; [HI] is the concentration of HI which stoichiometrically removes H and produces  $H_2 + I$ , according to eqn (2). Therefore, the slopes of the plots in fig. 3 correspond to  $(k_{H_2} - k_H + k_I)$  and the intercepts to  $k_{1st}^\circ = A + k_{H_2}[H_2]_0 + k_H[H]_0$ . The values of  $k_{1st}^\circ$  were obtained by extrapolation back to [HI] = 0;  $k_{1st}^\circ - k_{H_2}[H_2]_0$  is then plotted against  $[H]_0$  in fig. 4. Apart from the changes already described and allowed for, the experimental conditions were the same in each series of experiments contributing to fig. 3, so A should be constant and the slope of the line in fig. 4 yields

$$k_{\rm H} = (4 \pm 2) \times 10^{-14} \,{\rm cm}^3 \,{\rm molecule}^{-1} \,{\rm s}^{-1}$$

where the error limits are the standard error in the slope of the line in fig. 4, calculated with individual points weighted according to their standard error. The error of each point arises mainly from the standard error in the value of  $k_{1st}^{\circ}$  obtained from fig. 3. Errors in  $k_{\rm H_2}[{\rm H_2}]_0$  were also taken into account but are very small in comparison.



**Fig. 4.** The intercepts in fig. 3 are used to plot  $k_{1st}^{\circ} - k_{H_2}[H_2]_0$  against concentration of H atoms; the slope yields  $k_{H}$ . H atoms were produced in a microwave discharge and were titrated using NO<sub>2</sub>.

The only previous estimate of  $k_{\rm H}$  was made by Donohue and Wiesenfeld.<sup>40</sup> They observed non-exponential decay of I\* concentrations produced by the flash photolysis of HI, and attributed this behaviour to quenching by H atoms which were simultaneously being consumed by reaction with HI. Our results show clearly that this cannot be the explanation for the observation of Donohue and Weisenfeld. A possible alternative is that the reaction between H and HI produced significant concentrations either of I\* or of vibrationally excited H<sub>2</sub> which could re-excite I atoms by the reverse of process (9).

The rate constant obtained for quenching of I\* by H atoms corresponds to a thermally averaged collisional probability of *ca.*  $10^{-4}$  at 298 K. Quenching must involve non-adiabatic transitions between one or both of the potential-energy curves which correlate with  $H(^2S) + I^*(5\,^2P_{1/2})$  and the curves correlating with  $H(^2S) + I(5\,^2P_{3/2})$ . Of the total of seven states<sup>41</sup> [ $^{1}\Sigma^{+}$ ,  $^{1}\Pi(1)$ ,  $^{3}\Sigma^{+}$ ,  $^{3}\Pi(0^{+})$ ,  $^{3}\Pi(0^{-})$ ,  $^{3}\Pi(1)$ ,  $^{3}\Pi(2)$ ] that correlate with  $H(^2S) + I(^2P_J)$ , apparently only the  $^{1}\Sigma^{+}$  ground state is bound. The form of some of the other curves have been deduced from measurements using photofragment spectroscopy within the broad continuous absorption of HI between *ca.* 200 and 300 nm.<sup>42,43</sup> By determining the relative I: I\* yields and the angular anisotropy of the product scattering, such experiments allow one to decompose the overall absorption strength at any particular wavelength into contributions from different, unbound, upper states. In this way, van Veen *et al.*<sup>43</sup> have constructed approximate potential-energy curves for the  $^{3}\Sigma^{+}$  and  $^{3}\Pi(0^{+})$  curves which correlate with  $H(^{2}S) + I^{*}(5\,^{2}P_{1/2})$  and the curves for  $^{1}\Pi(1)$  and  $^{3}\Pi(1)$  correlating with  $H(^{2}S) + I(5\,^{2}P_{3/2})$ .

The lowest-energy crossing between a curve correlating with  $H+I^*$  and one correlating with H+I is that between  ${}^{3}\Pi(0^+)$  and  ${}^{1}\Pi(1)$ . This occurs at *ca.* 2400 cm<sup>-1</sup> above the  $H+I^*$  asymptotic limit. Furthermore, van Veen *et al.*<sup>43</sup> report that 'these states do not interact'. It therefore seems that the quenching of I\* by H atoms at thermal-collision energies must involve both quantum-mechanical tunnelling (*i.e.* a poor 'overlap' of the translational wavefunction on the interaction potential) and a non-adiabatic transition between electronic states which are only very weakly coupled. Our measurements of the low efficiency of the quenching process affirm this interpretation.



Fig. 5. First-order decay coefficients plotted against concentration of Br<sub>2</sub>.

k	method <sup>a</sup>	ref.
$0.15 \pm 0.02$	FP(CF <sub>3</sub> I)/PP	21
$2.2 \pm 0.5$	$FP(CF_3I)/RA$	22
$6.0 \pm 0.4$	$PLP(i-C_3F_7I)/RE$	23
$5.2 \pm 0.3$	$PLP(C_3F_7I)/RE$	24
$5.6 \pm 0.2$	$FP(CH_3I)/RA$	25
$5.5 \pm 0.1$	DLE(I)/CL	present work

**Table 2.** Comparison of rate constants  $(k/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$  at room temperature for quenching of  $I^*(5\,^2P_{1/2})$  by Br<sub>2</sub>

<sup>a</sup> See table 1.

Quenching of  $I^*(5\ ^2P_{1/2})$  by molecular and atomic halogens

The slight but definite positive gradients in the plots of  $k_{1st}$  against [HI] in fig. 3 should, according to the analysis given earlier, correspond to  $(k_{H_2}-k_H+k_I)$ . Therefore, it should be possible to derive a value for  $k_I$ . Unfortunately, very small, steady-state, concentrations of I<sub>2</sub> formed by heterogeneous recombination of iodine atoms might be present and these concentrations would rise as the amount of HI was increased so that [H] fell. I<sub>2</sub> is a very effective quencher of I\* atoms,<sup>24</sup> so that even a very small fractional concentration of molecular iodine could have a large effect. As a result, we prefer to analyse the data in fig. 3 to give only an upper limit to the rate constant for quenching by I atoms:  $k_I \le 5 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

Experiments designed to measure the rates of quenching of  $I^*$  by  $Br_2$  and  $Cl_2$  were carried out in a similar manner to those described for  $H_2$  (see also the Experimental section). The results for added  $Br_2$  are shown in fig. 5. The gradient

of this line yields  $k_{Br_2} = (5.5 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . As table 2 shows, this value is in excellent agreement with those determined in previous experiments.

Two series of experiments were performed with added Cl<sub>2</sub>. They gave linear plots of  $k_{1st}$  with Cl<sub>2</sub> and slopes corresponding to  $(4.8\pm0.8)\times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This rate constant is substantially lower than three values for  $k_{Cl_2}$  that have been reported previously:  ${}^{21,22,24}(2.1\pm0.3)\times 10^{-13}$ ,  $(1.3\pm0.1)\times 10^{-13}$  and  $(1.7\pm0.2)\times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

However, during the course of our own work we have become aware of three new measurements of this rate constant, yielding<sup>5-7</sup>  $(1.7 \pm 0.1) \times 10^{-14}$ ,  $(2.0 \pm 0.1) \times 10^{-14}$  and an upper limit of  $8 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Hall *et al.*<sup>7</sup> have given a very careful and convincing account of the difficulties which arise in trying to measure this small rate constant accurately. In particular, small concentrations of ICl and (they hypothesise) of Cl, which are formed in the reaction of I<sup>\*</sup> with Cl<sub>2</sub>, may introduce large systematic errors in the analysis as they are both rapid quenchers of I<sup>\*</sup>. Our system is perhaps particularly susceptible to such errors with its moderately complex flowtube chemistry. The addition of relatively large concentrations of Cl<sub>2</sub> could be accompanied by the formation of small concentrations of much more effective quenchers. Therefore, our result should be regarded as only an upper limit: *i.e.*  $k_{Cl_2} \le 5 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, although it does provide further confirmation that earlier values of this rate constant were much too high. This conclusion is consistent with the successful operation of the oxygen-iodine chemical laser, despite the existence in the laser fuel of significant concentrations of Cl<sub>2</sub>.

To determine  $k_{\rm Br}$ , the rate constant for quenching of I\* by Br atoms, the results of six separate runs were analysed. In each, the flow of HBr or Br<sub>2</sub> was varied but was always kept so that atomic hydrogen was in excess. The results of one of these series of experiments are shown in fig. 6. The conditions in all six runs and the gradients obtained by plotting  $k_{1st}$  against [HBr] or 2[Br<sub>2</sub>] are listed in table 3. These gradients can be identified with  $k_{\rm Br} + k_{\rm H_2} - k_{\rm H}$  or  $k_{\rm Br} + \frac{1}{2}k_{\rm H_2} - k_{\rm H}$ , the second and third terms allowing for the production of H<sub>2</sub> and consumption of H in reactions (3) and (4). Correcting the gradients for these contributions and taking a simple average from the six runs yields  $k_{\rm Br} = (5.1 \pm 1.9) \times 10^{-13} \, {\rm cm}^3 \, {\rm molecule}^{-1} \, {\rm s}^{-1}$ .

We have carried out fewer experiments on the quenching of I\* in the presence of atomic chlorine, and report only a preliminary result for  $k_{Cl}$ . Two series of measurements were carried out in which  $Cl_2$  was added to a gas flow containing an excess of H atoms. Each of these runs yielded reasonable straight-line plots of  $k_{1st}$ against [Cl<sub>2</sub> added] ( $\approx$ [Cl]), but the gradients of these lines were not in very good agreement. The first set of experiments, with [Cl<sub>2</sub>] added  $\leq 1 \times 10^{14}$  cm<sup>-3</sup>, gave a slope = ( $k_{Cl} + k_{H_2} - k_H$ ) = (2.8 ± 0.3) × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; the second, with [Cl<sub>2</sub>] added  $\leq 5 \times 10^{14}$  cm<sup>-3</sup>, gave (1.2 ± 0.2) × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The correction, ( $k_{H_2} - k_H$ ), is negligible in this case, so the gradients of these lines should be effectively equal to  $k_{Cl}$ .

Our measurements confirm that Cl atoms, in contrast to H and Br, are extremely efficient quenchers of I\*. As suggested by Hall *et al.*,<sup>7</sup> this must be at least part of the reason why earlier measurements, relying on photolysis to generate I\* atoms, were in error. In the work of Hoffman and Leone,<sup>24</sup> simultaneous photodissociation of Cl<sub>2</sub> would have occurred and introduced systematic error. Now that it is realised that Cl atoms quench I\* orders-of-magnitude more rapidly than Cl<sub>2</sub>, it will be possible to devise photochemical experiments to measure  $k_{Cl}$  more accurately than we feel is possible by our present method. We intend to perform such experiments and report on their results in the future. In the meantime, we quote a value of  $k_{Cl} = (2 \pm 1) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, where the error limits cover the difference





Fig. 6. First-order decay coefficients plotted against concentration of HBr. There is an excess of H atoms present and the HBr is therefore stoichiometrically converted to Br atoms; the slope yields  $k_{\rm Br}$ .

**Table 3.** Conditions and results of six series of experiments designed to measure the rate constant for quenching of I\* by Br atoms

precursor	$F_{\rm H_2}/\mu{ m mol}{ m s}^{-1}$	p/Torr	gradient <sup>a</sup>	$k_{ m Br}^{\ a}$
HBr	90	4.57	$5.9 \pm 0.5$	$5.3 \pm 0.5$
HBr	77	4.50	$4.7 \pm 0.5$	$4.1 \pm 0.5$
HBr	76	4.36	$3.8 \pm 0.5$	$3.2 \pm 0.5$
HBr	75	4.45	$5.1 \pm 0.7$	$4.5 \pm 0.7$
HBr	75	4.48	$7.6 \pm 0.5$	$7.0 \pm 0.5$
Br <sub>2</sub>	44	4.29	$6.7 \pm 1.4$	$6.6 \pm 1.4$

<sup>*a*</sup> In  $10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

between the two measurements that we have made. This value appears to be consistent with the value of  $k_{Cl}$  that Hall *et al.*<sup>7</sup> feel is necessary in order to explain the systematic error in the results of Hoffman and Leone.<sup>24</sup>

The relative rates of I<sup>\*</sup> quenching by halogen atoms (X) and halogen molecules (X<sub>2</sub>) show a remarkable change along the sequence X = Cl; Br; I:  $(k_X/k_{X_2}) \ge 2500$ ;  $9 \times 10^{-3}$ ;  $\le 1 \times 10^{-2}$ . Following Wiesenfeld and Wolk,<sup>25</sup> Hall *et al.*<sup>7</sup> have discussed why Cl<sub>2</sub> might be a much less effective quencher than Br<sub>2</sub> or I<sub>2</sub> in terms of the potential-energy pathway for sideways attack of I<sup>\*</sup> on X<sub>2</sub>. In principle, the reason for the difference in atomic quenching efficiencies: *i.e.*  $k_{Cl} \gg k_{Br} \approx k_1$ , should be easier to understand.

Unfortunately, the form of the relevant potential curves, at least those correlating with  $I^*+Cl$  and  $I^*+Br$ , are unknown. The existence of a state correlating with  $I^*+X$  which is not strongly repulsive is a necessary but not sufficient condition for efficient quenching. It would lead to a low-energy pathway for quenching, but the non-adiabatic transition probabilities during collisions will depend on the strength of the coupling between the two electronic states and the form of the curves at the crossing (or avoided crossing) point. Thus the  $B^{3}\Pi(0^{+}_{u})$  state of I<sub>2</sub> is quite strongly bound and crossed by repulsive curves leading to I( $5^{2}P_{3/2}$ ) + I( $5^{2}P_{3/2}$ ). However, the rate of predissociation from levels close to the dissociation limit of this state is known to be small, so the likelihood of non-adiabatic quenching transitions from this state during collisions should also be small.

Faist and Bernstein<sup>8</sup> have considered the correlations of electronic states in IBr for both the  $[\Lambda, S]$  coupling of Hund's case (a) and the  $[\Omega]$  coupling of case (c). They demonstrate that the lowest state correlating with  $I^* + Br$  is of  $0^+$  symmetry in case (c) and arises from an electronic configuration  $(\sigma)^2(\pi)^4(\pi^*)^2(\sigma^*)^2$ . Other states arise from combination of  $I + Br^*$  and I + Br, and interaction of two of these causes predissociation in the B state of IBr. It appears plausible that the quenching of  $I^*$  atoms by Cl or Br arises as a result of transitions between the  $0^+$  state populated in  $I^* + X$  collisions and the repulsive branches of the  $0^+$  curves leading to lowerenergy fragments. It may be that the wider gap between the asymptotic limits for  $I^* + Cl$  and  $I + Cl^*$  compared with that for X = Br leads to a more favourable disposition of these potential-energy curves.

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