Reaction Probabilities for the Reactions of Hydrogen Atoms at Selected Initial Energies in Hydrogen Iodide-Iodine Mixtures

John E. Nicholas* and Ghanshyam Vaghjiani

Chemistry Department, King's College, Strand, London WC2R 2LS

The reactions of photochemically generated H atoms formed at selected initial energies in $HI-I_2$ mixtures have been investigated. A kinetic analysis of reaction rates in systems with and without added I_2 allowed the measurement of integrated reaction probabilities for the reaction

$$H + HI \rightarrow H_2 + I.$$

At initial H atom energies of 49 and 106 kJ mol⁻¹ the respective reaction probabilities were 0.11 ± 0.02 and 0.35 ± 0.02 . At 178 kJ mol⁻¹, after allowance for partial photolytic yield of electronically excited I atoms, a reaction probability close to unity is indicated. In each set of experiments the analysis also yielded the ratio of thermal rate constants for reactions of H atoms with I₂(k_6) and HI(k_3) as 11.6±0.4. The reaction probabilities are discussed with particular reference to the very high values found in earlier work for other H atom + hydrogen halide reactions.

The earliest work in which reactions of H atoms of high translational energy were identified involved the photolysis of hydrogen halide-halogen mixtures with 254 nm radiation.¹⁻³ In such systems it is possible to study the relative reactivity of H atoms with hydrogen halide and with halogens and also the probability of reaction in H+ hydrogen halide collisions. Where the H atoms are formed at a selected initial energy it is possible to measure the relative probability of reaction or energy transfer on collision with reactant molecules over the energy range from initial H atom energy to the reaction threshold. This quantity is usually called the integral reaction probability, but although it has been measured for many H+hydrocarbon reactions over a wide energy range⁴ it has been determined for only a limited number of cases with H+hydrogen halide reactions. For H+HCl \rightarrow H₂+Cl the integral reaction probability was found to be 0.82 and 0.55 at initial atom energies of 203 and 118 kJ mol⁻¹, respectively,⁵ with 0.61 for the D+DCl reaction at 203 kJ mol^{-1.6} For H+HBr a reaction probability of 1 was indicated over the energy range 108-286 kJ mol^{-1.5,7,8} For the HI+I₂ or DI+I₂ systems, however, no reaction probabilities have been reported.

In studies of relative reactivity, the ratio of rate coefficients for reaction with HCl and Cl₂ have been measured for thermal H atoms⁵ and for atoms at an initial energy of 203 kJ mol⁻¹,⁸ and similar measurements have been carried out for D atoms.⁶ There are analogous results for H atoms reacting with HBr and Br₂,⁷ and in the deuterated system⁸ at initial energies of 108 and 286 kJ mol⁻¹. For reactions of H atoms with I₂ and HI, ratios of rate coefficients have been measured either for translationally excited atoms, or in highly moderated systems where the atoms react at thermal energies.^{2,3,9-13}

There continues to be general interest in studies of reactants with non-equilibrium energy distribution and in measurement of the appropriate rate parameters. We report here a study of the reactions of H atoms at selected initial energies in HI alone, compared with H atoms in $HI-I_2$ mixtures. For the comparative systems a kinetic analysis relates their relative H_2 yields, measured by mass spectrometry, to the integrated reaction

Reaction Probabilities for H in HI-I₂ Mixtures

probabilities for the H+HI reaction, which were thereby determined for the first time at several initial atom energies. In addition, it was possible to deduce the ratio of rate coefficients for the reaction of thermal H atoms with HI and with I_2 . Such information is a prerequisite for the study of H atom reactions with hydrocarbons by a route that will avoid the general limitation to isotopically mixed reactants.⁴

Experimental

HI was prepared by the action of H_3PO_4 (analytical grade, specific gravity 1.75, Fison) on KI (analytical grade, Fison) with gentle heating. The reagents were refluxed under dry N₂ and the HI evolved was carried through to a trap at *ca*. 263 K and finally frozen in a second trap at 77 K. The HI was transferred to the vacuum line and passed over P₂O₅ several times to dry it and was then treated with red phosphorus to remove I₂. Further purification by freeze-thaw cycles between 193 and 77 K gave a white solid at 77 K. The purified HI was stored in a darkened Pyrex cell attached to the line at 77 K. U.v. spectra of samples showed >99% purity with no detectable I₂. The HI was purified from time to time as required during the course of the study. H₂ and He were supplied by Air Products (99.9%). I₂ (analytical grade, Fisons) was distilled in the vacuum system prior to use.

Gas mixtures were prepared on a greaseless vacuum line with a background pressure of 10^{-5} Torr[†] (measured on a Penning gauge). Reagent pressures were measured with an MKS baratron gauge or on an all-glass spiral gauge. HI pressures employed were in the range 4-80 Torr and photolyses were carried out in pairs in identical vessels. One vessel had no added I₂ and was maintained at 273 K to restrict the pressure of any I₂ generated to a maximum of 0.03 Torr. The other vessel, at 297 ± 1 K contained the same pressure of HI, with I₂ added to give a pressure 0.300±0.005 Torr. In all runs a trace of He was added as an internal calibrant for subsequent mass-spectrometric analysis. Photolysis cells were kept optically dark, with a retractable shutter on the quartz window, and were aged for several days in HI-I₂ before use. Frequent dark runs showed that there was no significant formation of H₂ in the absence of radiation. The extent of photolysis was generally kept below 1.0%.

The radiation source was a super-pressure mercury arc (Bausch and Lomb SP 200) in conjunction with a Bausch and Lomb monochromator (33-86-07, 1200 grooves per mm) used with transmitted band widths of up to 10 nm. After an initial warming-up time the light output remained steady for long periods, and a specially constructed cell holder ensured reproducible alignment for all runs. At the wavelengths employed the initial laboratory translational energy $E_{\rm L}$ of the H atom can be calculated from the photon energy, $E_{\rm p}$, the dissociation energy at 0 K, D_0 , and the mean rotational energy, $E_{\rm r}$, from the standard relationship $E_{\rm L} = (E_{\rm p} - D_0 + E_{\rm r})M_{\rm I}/M_{\rm HI}$. Thus more than 99% of the available excess energy appears as translational energy of the H atom. The wavelengths used in this work were 254, 300 and 350 nm, corresponding to initial H atom energies of 178, 106 and 49 kJ mol⁻¹, respectively.

After photolysis the cell was cooled to 77 K and the non-condensible gases, He calibrant and H_2 photolysis product were analysed by mass spectrometry. The quadrupole mass spectrometer (V. G. Mass Torr F) was directly calibrated with He-H₂ mixtures over the range of pressures experienced in the photolysis experiments.

Results and Discussion

Experiments with and without added I_2 , referred to henceforth as scavenged and unscavenged systems, were carried out at each of a series of HI pressures in the range

†1 Torr ≈133.3 Pa.

J. E. Nicholas and G. Vaghjiani



Fig. 1. Relative rates of H₂ formation in scavenged and unscavenged experiments, R_s/R_u , vs. $\{1 + k_6[I_2]/(k_3[HI])\}^{-1}$ for three initial H atom energies: \bigcirc , 178 kJ mol⁻¹; \blacksquare , 106 kJ mol⁻¹; \square , 49 kJ mol⁻¹. The lines were plotted according to the computational procedure described in the text.

4-80 Torr. At a given HI pressure, analysis of the H_2 yield with increasing photolysis time showed a linear increase of product concentration with time, *i.e.* a steady rate for the period covered, up to 1% photolysis. Reproducibility in repeated experiments was $ca. \pm 5\%$. At each HI pressure the product yield in unscavenged experiments exceeded those in scavenged runs, and fig. 1 shows the ratio of rates for H_2 formation in scavenged and unscavenged runs plotted in a form suggested by the kinetic analysis described below.

The following reaction mechanism applies when $HI-I_2$ mixtures are photolysed with u.v. radiation. In the range 250-350 nm the absorption coefficients¹⁴ and concentrations of HI and I_2 are such that virtually all absorption of radiation is by HI.

HI $\xrightarrow{h\nu}$ H*+I

 $H^* + HI \rightarrow H_2 + I \tag{1}$

$$H^* + HI \rightarrow H + HI \tag{2}$$

$$H + HI \rightarrow H_2 + I \tag{3}$$

$$H^* + I_2 \rightarrow HI + I \tag{4}$$

$$\mathbf{H}^* + \mathbf{I}_2 \to \mathbf{H} + \mathbf{I}_2 \tag{5}$$

$$H+I_2 \rightarrow HI+I \tag{6}$$

$$2I + M \rightarrow I_2 + M \tag{7}$$

H^{*} represents translationally excited hydrogen atoms, and H those atoms which have been moderated in non-reactive collisions to thermal energies. The possible production from HI of electronically excited I atoms at the highest quantum energy studied is discussed below. For translationally excited species the rate coefficients k_1 , k_2 , k_4 and k_5 represent an average probability over the energy range from the initial energy to the threshold for the process. For thermalised H atoms, k_3 and k_6 will be the conventional reaction rate constants.

In photochemical studies of translationally excited atoms the most useful kinetic coefficient is the fraction of atoms that undergo reaction on collision with the reactant

Reaction Probabilities for H in HI-I₂ Mixtures

species over the energy range from the initial atom energy to the reaction threshold. This is designated the integrated reaction probability, $P_{IR} = \bar{k}_1/(\bar{k}_1 + \bar{k}_2)$. The other quantity of interest here is the relative reactivity of I₂ and HI, expressed by the ratio of rate constants k_6/k_3 . Both this ratio and P_{IR} at the selected initial energy may be obtained employing a kinetic analysis which gives an expression for the relative reaction rates in the scavenged and unscavenged experiments as a function of HI and I₂ concentration. The rate of formation of H₂ may be derived from the mechanism employing a simple steady-state treatment for the concentration of thermalised H atoms. Martin *et al.*¹⁵ have shown that in photochemical hot atom systems behaviour predicted by steady-state treatments is followed over a wide range of conditions.

If R_s is the rate of formation of H_2 in the scavenged experiments and R_u the unscavenged rate, then the treatment gives

$$\frac{R_{\rm s}}{R_{\rm u}} = \frac{\bar{k_1}}{\bar{k_1} + \bar{k_2}} + \frac{\bar{k_2}}{\bar{k_1} + \bar{k_2}} \left(1 + \frac{k_6[\rm I_2]}{k_3[\rm HI]}\right)^{-1}$$

and since $P_{\rm IR} = \bar{k_1} / (\bar{k_1} + \bar{k_2})$

$$\frac{R_{\rm s}}{R_{\rm u}} = P_{\rm IR} + (1 - P_{\rm IR}) \left(1 + \frac{k_6 [\rm I_2]}{k_3 [\rm HI]} \right)^{-1}.$$
 (1)

The derivation leading to eqn (1) involves the approximation that $(\bar{k}_1 + \bar{k}_2)[\text{HI}] \gg (\bar{k}_4 + \bar{k}_5)[\text{I}_2]$, *i.e.* that the frequency of collisions of H* with HI greatly exceeds those with I₂ over the energy range studied. The ratio $(\bar{k}_1 + \bar{k}_2)/(\bar{k}_4 + \bar{k}_5)$ will be similar to the ratio of average values over the energy range of the total collisional cross-sections for H with HI and I₂, and these should not differ greatly (the ratio of hard-sphere cross-section areas is 0.77).¹⁶ Thus with HI present in such large excess (*ca.* 15–150 fold) the above inequality represents a reasonable assumption.

Eqn (1) shows that a graph of the relative rates R_s/R_u against $\{1 + k_6[I_2]/(k_3[HI])\}^{-1}$ should be a straight line with intercept equal to P_{IR} and slope $(1 - P_{IR})$ at the selected initial energy. It is possible by a straightforward computational procedure to test that the experimental data are consistent with eqn (1). The computations also yield the best value for the ratio k_6/k_3 and for P_{IR} at that energy since, if there is consistency, not only must there be a linear plot but the relationship, slope = 1 - intercept, must also hold. Taking a trial value of k_6/k_3 the value of $\{1 + k_6[I_2]/(k_3[HI])\}^{-1}$ was calculated for each R_s/R_u value. A least-squares treatment then gave the calculated slope, S_c , and intercept, I_c . The value of $\{1 + k_6[I_2]/(k_3[HI])\}^{-1}$ must tend to unity as the HI pressure tends to infinity and this is incorporated as a fixed point. There will be only one value of k_6/k_3 for which $S_c - (1 - I_c) = 0$. Generally $S_c - (1 - I_c)$ will be a finite number, d. A new value of k_6/k_3 will give a different value of d and if this is closer to zero there is a closer approximation to the best k_6/k_3 . A BBC microcomputer was programmed to calculate the best value of k_6/k_3 . Starting with a trial value, the program iteratively converged the ratio until the condition d = 0 was satisfied to better than 0.01. The best results at each of the three initial H atom energies are shown in fig. 1. The corresponding values for k_6/k_3 and P_{IR} at each energy are given in table 1 with errors derived from the standard deviation on the slope and intercept.

A satisfactory feature of the calculations was that the best value of the ratio k_6/k_3 was constant as energy varied. These are thermal rate constants which should be independent of the behaviour of the translationally excited atoms at each initial energy. The value of 11.6 is consistent with the ratios (in the range 10-12 with errors of up to 20%) determined in conventional thermal and highly moderated photochemical systems, 9,10,12,13 whereas the ratio of rate parameters for excited H atoms may fall to $3.5.^2 k_6$ and k_3 have also been measured separately¹⁷ by a discharge flow technique giving a value of $k_6/k_3 = 21.6 \pm 11.4$ at 298 K. The linear plots shown in fig. 1 and the

J. E. Nicholas and G. Vaghjiani

initial H atom energy /kJ mol ⁻¹	k_{6}/k_{3}	$P_{\rm IR}$
178	11.6 • 0.6	0.65 ± 0.03
106	11.7 ± 0.4	0.34 ± 0.02
49	11.5 ± 0.6	0.11 ± 0.02

Table 1. Values of P_{IR} and k_6/k_3 at each initial H atom energy studied

constant value of k_6/k_3 provide significant support for the proposed reaction mechanism and the kinetic analysis leading to eqn (1). The main category of reactions of translationally excited H atoms investigated by photochemical techniques is with alkanes.⁴ The general use of mass-spectrometric detection always limits such studies to isotopically mixed systems, H+RD or D+RH. With the relative reactivity of HI and I₂ towards thermal H atoms established here, together with similar data for alkyl radicals, the I₂ scavenging of radical fragments should allow the measurement of reaction probabilities for isotopically pure H+RH reactions.

 P_{IR} values for reaction (1) have been obtained for the first time. They show a high probability of reaction, decreasing with energy. The P_{IR} values are, for example, several times higher than those found for the total probability of abstraction reaction from C—H bonds in alkanes.⁴ The fall in P_{IR} with energy from 178-49 kJ mol⁻¹ is consistent with a threshold energy close to zero, which is not unexpected for a reaction of exothermicity 137 kJ mol⁻¹. It should be noted that extrapolation of such data to zero P_{IR} yields the 'phenomenological' threshold energy, though for such low threshold reactions this should be close to the true threshold. The highest reported value for the Arrhenius activation energy is 18.8 kJ mol^{-1,3} but a later estimate of zero activation energy¹⁰ seems more reasonable.

A more interesting comparison for the P_{IR} data is with those previously reported for H atom reactions with HCl and HBr. In photochemical studies, where product yields were determined by spectroscopic absorbance of halogen molecules or from absolute measurement of residual hydrogen gas pressure employing Toepler pump, McLeod gauge and sample combustion, P_{IR} values were: for HCl, 0.82-0.55 in the energy range 203-116 kJ mol^{-1,5} and for HBr, 1, over a similar energy range.^{5,7,8} Thus for HBr all H atoms reacted before reaching thermal energies and moderating collisions with HBr are ineffective. This trend suggests that unit reaction probabilities might also be expected for the H+HI reaction, but that has not been found in the present work. Unit probability, in terms of the present kinetic analysis, corresponds to $(k_1 + k_2) \approx k_1$, or $k_2 \approx 0$. For the plot in fig. 1, this would mean all data points lying parallel to the abscissa with $R_s/R_u = 1$ at all [HI]/[I₂] ratios, *i.e.* $R_s = R_u$, since all H atoms would react before thermalisation. The interpretation of the data at highest energy is complicated by the possibility of excited I atoms being formed in the photolysis, as discussed below.

Some approximate, but suggestive comparisons may be made on the basis of relevant cross-sections. For H+HCl Jardine *et al.*⁵ have estimated that the average cross-section is 0.007 nm² up to 200 kJ mol⁻¹, compared with a total (hard-sphere) collisional cross-section of 0.27 nm.² Dubrin and coworkers found a reaction cross-section for abstraction from sec-C-D in the H+C₄D₁₀ reaction¹⁸ which has a maximum value of 0.0035 nm² at 110 kJ mol⁻¹ and an average value from the threshold to 200 kJ mol⁻¹ of *ca.* 0.003 nm². The total collisional cross-section is somewhat higher (0.44 nm²) than for HCl. The lower relative reaction probability is reflected in lower P_{1R} values in C₄D₁₀ than in HCl. Dubrin's work also provides some insight into the H+HBr reaction. From data in highly Xe moderated HBr C₄D₁₀ mixtures it was possible to deduce the relative values

Reaction Probabilities for H in HI-I₂ Mixtures

of rate coefficients for reactive collisions of H with HBr and with C_4D_{10} .¹⁹ This allowed the calculation of the average value of the reaction cross-section for H+HBr over the energy range 35-170 kJ mol⁻¹. A result of 0.016 nm² was obtained and when related to the total collision cross-section in this case it indicates that the reaction probability for HBr is indeed greater than that for HCl, though perhaps not so much higher as to suggest unit P_{IR} values in the photochemical HBr system. Furthermore Dubrin and coworkers found the relative value of rate coefficients for reaction of H atoms with HBr and with C_4D_{10} and these can be converted to relative values of P_{IR} . If the rate coefficients for these reactions are $\bar{k}(HBr)$ and $\bar{k}(C_4D_{10})$ and the coefficients for moderating collisions are $\bar{k}_m(HBr)$ and $\bar{k}_m(C_4D_{10})$ then

$$\frac{P_{IR}(HBr)}{P_{IR}(C_4D_{10})} = \frac{\bar{k}(HBr)}{\bar{k}(C_4D_{10})} \frac{[\bar{k}(C_4D_{10}) + \bar{k}_m(C_4D_{10})]}{[\bar{k}(HBr) + \bar{k}_m(HBr)]}$$
(2)

The terms in square brackets in eqn (2) represent the total probability of collision with C_4D_{10} and HBr. The ratio of these probabilities corresponds to the ratio of total collisional cross-sections over the experimental energy range and this ratio should, to a good approximation, equal that for (energy independent) hard-sphere cross-sections.¹⁶ Thus Dubrin's results for the relative rate coefficients for reaction and $P_{IR}(C_4D_{10})$ leads to $P_{IR}(HBr)$ values of 0.7-0.8 in the energy range 100-200 kJ mol⁻¹. Thus there may be a small discrepancy between the results for photochemical H atom studies employing mass-spectrometric analysis of product ratios and those with absolute measurement of residual gas pressures with classical manometric and combustion methods. High reaction cross-sections for H atom reactions with hydrogen halides, combined with inefficient moderation in elastic collisions, will give very high P_{1R} values in photochemical systems. If only elastic collisions are involved in moderation, the fractional energy loss will be very small and P_{1R} values tending to unity might be predicted for HBr and HI. However, there may well be an inelastic contribution in moderating collisions. Vibrationaltranslational energy transfer is known to be efficient in the hydrogen halides themselves²⁰ and for H-hydrogen halide inelastic transfer this should be most efficient in HI where rovibrational levels are significantly closer than for the other hydrogen halides.²¹ This may lead to P_{IR} values which, though high, are less than unity, especially at the lower energies here.

The interpretation of results at the highest energy studied is complicated by the possibility that at the wavelength of radiation employed a fraction of the dissociation taking place yields I atoms in the ${}^{2}P_{1/2}$ electronically excited state. This in turn means that there is less excess energy to be partitioned as translational energy of the separating atoms. Thus, instead of the H atoms exclusively possessing 178 kJ mol⁻¹, a certain fraction will be formed with 87 kJ mol⁻¹ energy. Reports of the fraction of excited I atoms formed vary from 0.07 to $0.55.^{22-27}$ Taking a relatively high value of 0.5, and a P_{IR} at 87 kJ mol⁻¹ interpolated from our data, a simple calculation indicates that P_{IR} at 178 kJ mol⁻¹ should be close to unity. Thus at the higher energy this reaction gives a similar, very high reaction probability to that previously found for the H+HBr reaction.^{5,7,8}

We thank the S.E.R.C. for a Research Studentship held by one of us (G.V.) during the tenure of which this work was carried out.

References

- 1 R. A. Ogg Jr and R. R. William Jr, J. Chem. Phys., 1945, 13, 586.
- 2 R. R. William Jr and R. A. Ogg Jr, J. Chem. Phys., 1947, 15, 691.
- 3 H. A. Schwarz, R. R. William Jr and W. H. Hamil, J. Am. Chem. Soc., 1953, 74, 6007.
- 4 G. A. Oldershaw, Gas Kinetics and Energy Transfer (Royal Society of Chem., London, 1977), vol. 2, p. 96.

J. E. Nicholas and G. Vaghjiani

- 5 D. K. Jardine, N. M. Ballash and D. A. Armstrong, Can. J. Chem., 1973, 51, 656.
- 6 G. O. Wood and J. M. White, J. Chem. Phys., 1970, 52, 2613.
- 7 R. A. Fass, J. Phys. Chem., 1970, 74, 984.
- 8 R. A. Fass, J. W. Hoover and L. M. Simpson, J. Phys. Chem., 1972, 76, 2801.
- 9 J. L. Holmes and P. Rodgers, Trans. Faraday Soc., 1968, 2348.
- 10 J. H. Sullivan, J. Chem. Phys. 1962, 36, 1925.
- 11 K. F. Bonhoeffer and L. Farkas, Z. Phys. Chem., 1928, 132, 235.
- 12 R. D. Penzhern and B. De B. Darwent, J. Phys. Chem., 1968, 72, 1639.
- 13 R. J. Letelier, H. L. Sandovral and R. D. Penzhorn, J. Phys. Chem., 1971, 75, 835.
- 14 H. Okabe, Photochemistry of Small Molecules (Wiley-Interscience, New York, 1978).
- 15 R. M. Martin, L. E. Compton and G. D. Beverley, J. Phys. Chem., 1974, 78, 559.
- 16 J. O. Hirschfelder, C. F. Curtiss and R. R. Bird, Molecular Theory of Gases and Liquids (John Wiley, New York, 1954).
- 17 K. Lorenz, H. G. Wagner and R. Zellner, Ber. Bunsenges. Phys. Chem., 1979, 83, 55.
- 18 R. G. Gann, W. M. Ollison and J. Dubrin, J. Chem. Phys., 1971, 54, 2304.
- 19 R. G. Gann and J. Dubrin, J. Phys. Chem., 1972, 76, 1321.
- 20 J. T. Yardley, Introduction to Molecular Energy Transfer (Academic Press, New York, 1980).
- 21 G. Herzberg, Molecular Spectra and Molecular Structure I, Spectra of Diatomic Molecules (Van Nostrand, Princeton, New Jersey, 2nd edn, 1950).
- 22 G. A. Oldershaw, D. A. Porter and A. Smith, J. Chem. Soc., Faraday Trans. 1, 1972, 68, 2218.
- 23 L. E. Compton and R. M. Martin, J. Phys. Chem., 1969, 73, 3474.
- 24 R. J. Donovan and D. Husain, J. Chem. Soc., Faraday Trans. 1, 1966, 62, 11.
- 25 P. Brewer, P. Das, G. Ondrey and R. Bersohn, J. Chem. Phys., 1983, 79, 720.
- 26 R. D. Clear, S. J. Riley and K. R. Wilson, J. Chem. Phys., 1975, 63, 1340.
- 27 G. N. A. Van Veen, K. A. Mohamed, T. Baller and A. E. de Vries, Chem. Phys., 1983, 80, 113.

Paper 5/1156; Received 9th July, 1985