## KINETIC STUDY OF THE H + IBr REACTION: RATE CONSTANTS, BRANCHING RATIO AND YIELDS OF EXCITED HALOGEN ATOMS

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The total rate constant for the reaction  $H + IBr \rightarrow HI + Br^{-}(Br) \ HBr + I^{-}(I) \ (1.5 \pm 0.04) \times 10^{-10} \ cm^{3}/s$  has been obtained at room temperature. The reaction path leading to bromine-atom formation was found to be predominant ( $\approx 90\%$ ). Our results together with data on the rate constants for the H-atom reactions with halogen and interhalogen (two branches) molecules show that the rate constants for such reactions are determined exclusively by H-atom interaction with the attacked halogen atom and are nearly independent of the other halogen in the molecule. The rate constants for the Br<sup>+</sup>( $^{2}P_{1/2}$ ) collisional deactivation by H<sub>2</sub>S and CF<sub>3</sub>Br have been measured as ( $6.2 \pm 1.6$ ) × 10<sup>-13</sup> and ( $1.2 \pm 0.3$ ) × 10<sup>-13</sup> cm<sup>3</sup>/s respectively

## 1 Introduction

The fast atomic exchange reactions in which spinorbit excitation of halogen atoms is energetically possible have been much studied recently [1-5]. These reactions are of interest because they could be sources for the excited atoms in chemical lasers acting on the  ${}^{2}P_{1/2} - {}^{2}P_{3/2}$  transition in halogen atoms Moreover, the reliable kinetic data for such simple reactions as H + IBr are important for insight into the reaction mechanism of fast atom--molecule reactions [1,2]. So far studies of reactions in which the <sup>2</sup>P<sub>1/2</sub> excited state of halogen atoms may be produced include  $I^* + Br_2$  [3],  $F + Br_2$  [3],  $F + I_2$  [5, 6] and H + I<sub>2</sub> [6]. For the first two reactions, the efficiency of the Br\* production was found to exceed the  $33_3^1\%$  needed to achieve population inversion [3] For the other two, the fractional yield of I\* was estimated to be less than 7% [5,6], though for F +  $I_2$  reaction a large I\* yield ( $\approx 90\%$ ) has been predicted on the basis of indirect data [4]

In the present work we have carried out a detailed study of the reaction  $(\Delta H_0 \text{ values in } kJ/mol \text{ are given in parentheses})$ 

$$H(^{2}S) + IBr \xrightarrow{k_{1}} \overset{\tau_{Br}}{\longrightarrow} HI + Br (-756)$$

$$H(^{2}S) + IBr \xrightarrow{k_{1}} \overset{\tau_{Br}}{\longrightarrow} HI + Br (-1197)$$

$$\overset{\epsilon_{I}}{\longrightarrow} HBr + I^{*} (-945)$$

$$1 - \epsilon_{I} \rightarrow HBr + I (-1856), (I)$$

which is of interest for at least two reasons. First, it has two reaction branches, the branch leading to iodine atoms being much more exothermic. Secondly, the energy released in this reaction is sufficient for the spin—orbit excitation of either I or Br.

We have measured the total rate constant,  $k_1$ , the probability for each branch,  $\eta_{Br}$  and  $\eta_I = 1 - \eta_{Br}$ , and estimated the fractional yields of excited atoms,  $\epsilon_{Br}$  and  $\epsilon_I$  The results obtained and some data for similar reactions are discussed in terms of the reaction mechanism and product energy distribution.

#### 2. Experimental

The time dependence of I (I\*) and Br (Br\*) concentrations produced upon short-pulsed broad-band flash photolysis of mixtures of H<sub>2</sub>S (a photolytic source of H atoms) with IBr, was measured Concentrations of iodine and bromine atoms in the  ${}^{2}P_{1/2}$ and  ${}^{2}P_{3/2}$  states were monitored at some time delay,  $t_{d}$ , upon photolysis by using the technique of laser atomic-resonance spectroscopy [7,8]. Pulsed photodissociation iodine and bromine lasers acting on the  ${}^{2}P_{1/2}$  (F' = 3) $-{}^{2}P_{3/2}$  (F = 4) and  ${}^{2}P_{1/2}$  (F' = 2) $-{}^{2}P_{3/2}$  (F = 3) transitions in the ground electronic states of iodine and bromine atoms, respectively, were used as the sources of probing beam.

The change, z, in the intensity of the probing beam upon n passings through the cell of the length l is related to the concentrations of atoms (denoted A\* for the  ${}^{2}P_{1/2}$  state and A for the  ${}^{2}P_{3/2}$  state) by the following equation [7,8]:

$$\ln z = \kappa g \sigma_{F'-F} nl(2[A^*] - [A]), \qquad (1)$$

where  $\sigma_{F'-F}$  is the stimulated-emission cross section of the laser transition in respective atom, g is the statistic weight equal to 7/24 for iondine and 5/16 for bromine atoms, the factor  $\kappa = 0.56$  takes into consideration the partial overlap of F' = 2-F = 3 lines for bromine isotopes <sup>79</sup>Br and <sup>81</sup>Br [8] (for iodine atom  $\kappa = 1$ ). For our case of low pressures,  $\sigma_{F'-F}$ , is equal to the value corresponding to the center of Dopplerbroadened lines at 300 K  $\sigma_{3-4}^{D} = 1.3 \times 10^{-17} \text{ cm}^2$ (todine) and  $\sigma_{2-3}^{D} = 1.0 \times 10^{-17} \text{ cm}^2$  (bromine) which are known from both calculated [9] and experimental data [7,8,10]. The admission of efficient quenchers of the  ${}^{2}P_{1/2}$  state (O<sub>2</sub> for I\* and CO<sub>2</sub> for Br<sup>+</sup>, with the rate constants of quenching  $2.7 \times$  $10^{-11}$  [7] and  $1.5 \times 10^{-11}$  cm<sup>3</sup>/s [11], respectively) may provide a complete relaxation at the moment  $t_{\rm d}$  Hence the attenuation of the probing beam,  $z_{\rm tot}$ , measured in such a case, is determined by the total concentration of atoms at the moment  $t_d$ ,  $[A_{tot}] =$ [A\*] + [A]

$$\ln z_{tot} = -\kappa g \sigma_{F'-F} n l [A_{tot}] . \qquad (2)$$

Thus the absolute total concentration of atoms can be determined from (2) as a function of  $t_d$ , and then from (1) and (2) a simple expression for the fraction of excited atoms,  $\epsilon$ , at the moment  $t_d$  could be denved<sup>-</sup>

$$\epsilon = [A^*]/[A_{tot}] = \frac{1}{3}(1 - \ln z / \ln z_{tot})$$
 (3)

The experimental apparatus is shown in fig 1. By using the multipass optical system, the probing laser beam was allowed to undergo n = 3 + 8m (m = 0, 1, 2 or 3) passes through the quartz cell (2 5 cm inner diameter and 100 cm length) Xenon-filled flashlamp ( $\approx 4 \,\mu \text{s}$  fwhm) was used to produce H(<sup>2</sup>S) atoms upon broad-band UV photolysis of  $\approx 0.5$  Torr H<sub>2</sub>S The experimental procedure, the parameters of photodissociation lasers used and other details have been reported elsewhere [3,7,8].

The desired IBr pressure in the cell ( $\approx 10^{-2}$  Torr) was maintained by cooling the cell side-arm containing IBr crystals IBr pressure in the range -50 to  $\pm 20^{\circ}$ C was determined by using the quartz capacitor pressure gauge In addition to H<sub>2</sub>S and IBr, 1 to 2 Torr of either O<sub>2</sub> or CO<sub>2</sub> (quenchers) or Ar (buffer gas) were admitted into the cell All the experiments were carried out at 296 K IBr was prepared by melting the stoichiometric amounts of I<sub>2</sub> and Br<sub>2</sub> preliminary degassed and sublimated (or distilled) in vacuum over P<sub>2</sub>O<sub>5</sub> All the gases used were passed over a liquid-nitrogen trap in vacuum.

#### 3 Results

The fast secondary reaction,

Br(<sup>2</sup>P<sub>3/2</sub>) + IBr 
$$\xrightarrow{k_2}$$
 Br<sub>2</sub> + I(<sup>2</sup>P<sub>3/2</sub>),  
 $k_2 = 3.5 \times 10^{-11} \text{ cm}^3/\text{s} [12]$ , (II)

in which the bromine atoms formed in reaction (1)



Fig 1 Experimental apparatus lodine or bromine laser, 1, quartz plate, 2, the mirrors of the multi-pass optical system, 3, quartz cell, 4, flash-lamp, 5; reflector, 6, photodetector, 7

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Fig 2 The concentrations of the Br (•) and I (•) atoms as a function of the delay time,  $r_d$ , upon the flash photolysis of the mixture (0 47 Torr H<sub>2</sub>S + (1 4 × 10<sup>-2</sup>) Torr IBr + 1.5 Torr O<sub>2</sub> (or CO<sub>2</sub>)) The sum of the I and Br atom concentrations is given by the heavy solid line

are converted into iodine atoms, may be important under our experimental conditions.

The measurements of  $k_1$  and  $\eta_{\rm Br}$  were carried out in the presence of quenchers Hence, the excited atomic states could be neglected, and according to eq (2) the  $z_{\rm tot}$  values measured gave total atomic concentrations. The observed kinetics of  $I({}^{2}P_{3/2})$  and  $Br({}^{2}P_{3/2})$  atoms is presented in fig. 2 Usually 6–8 measurements of  $z_{\rm tot}$  were performed at every  $t_d$  and averaged The results show that the reaction (I) gives mainly bromine atoms while the iodine atoms observed are produced in the secondary reaction (II) This conclusion is supported by the fact that the sum of the I and Br atom concentrations remains constant at  $t_d > 50 \,\mu$ s, when the faster reaction (I) is complete

The value of [I] attained at large  $t_d$  was independent of [IBr] This indicates the negligible role of both the direct IBr photolysis and the slow reaction  $H + H_2S$ , and supports the validity of the assumption [H]  $\leq$  [IBr] Hence, the [I] value at large  $t_d$  gives the  $H_2S$  photodissociation degree  $\alpha \approx 0.4\%$  Nevertheless, control measurements of  $\alpha$  were carried out under the same conditions using  $\approx 0.1$  Torr  $I_2$  instead of IBr. For the reaction

$$H + I_2 \xrightarrow{k_3} HI + I(^2P_{3/2})$$
(III)

the rate constant  $k_3$  is equal to  $(3.0 \pm 0.8) \times 10^{-10}$  cm<sup>3</sup>/s [6] The same value  $\alpha = 0.4\%$  was thus obtained.

Assuming an instant production of H atoms and taking into account a small ( $\approx 14\%$ ) consumption of IBr in processes (I) and (II), the rate constant  $k_1 =$  $(1.5 \pm 0.4) \times 10^{-10}$  cm<sup>3</sup>/s was found for reaction (I) The presence of equilibrium amounts of I<sub>2</sub> and Br<sub>2</sub> (4% at 300 K [13]) does not influence the  $k_1$ value since  $k_3$  is twice as large as  $k_1$ , and the rate constant for the reaction

$$H + Br_2 \xrightarrow{k_4} HBr + Br(^2P_{3/2}), \qquad (IV)$$

 $k_4 \ll k_1$ . However, in view of a small probability of the reaction branch leading to iodine atom formation, the reaction (III) may contribute significantly to the initial iodine atom concentrations observed. Taking into consideration this contribution, the probability of both branches for reaction (I) were obtained

$$\eta_{\rm Br} = 1 - \eta_{\rm I} = 0.89 \pm 0.08$$
.

It is worth mentioning that the presence of duluting gases  $(O_2, CO_2 \text{ or } Ar)$  in the cell prevented a noticeable temperature rise of gas mixture upon photolysis and from diffusion of atoms to the cell walls and their heterogeneous reactions

Our experimental technique allowed us to determine the efficiency of the excited atom production in reaction (I) For this purpose the quenching gases were replaced by Ar, and then z values were measured under conditions when other quenching processes were negligible. The published rate constant for the quenching of the  $I^*({}^2P_{1/2})$  state by IBr and  $H_2S$ , and of the  $Br^*({}^2P_{1/2})$  state by IBr are  $4.3 \times 10^{-12}$  [14],  $(1.5 \pm 0.4) \times 10^{-13}$  [6] and  $2 \times 10^{-12}$  cm<sup>3</sup>/s [3], respectively. The rate constant for the process

$$Br^{*}(^{2}P_{1/2}) + H_{2}S \xrightarrow{k_{5}} Br(^{2}P_{3/2}) + H_{2}S$$
 (V)

has been measured. Br\* atoms were produced by UV flash photolysis of CF<sub>3</sub>Br. From the observed time dependence of z and  $z_{tot}$ , we could determine both the fractional yield of Br\* upon the broad-band photolysis of CF<sub>3</sub>Br ( $\epsilon = 0.70 \pm 0.10$ ) and the rate constants for the Br\* quenching by CF<sub>3</sub>Br ( $k_{CF_3Br} =$  $(1.2 \pm 0.3) \times 10^{-13}$  cm<sup>3</sup>/s) To obtain the desired  $k_5$ value, 2 to 4 Torr of H<sub>2</sub>S were admitted to ≈4 Torr of CF<sub>3</sub>Br, and the  $z(t_d)$  value was measured. The results are presented in fig. 3 as a linear plot in coordi-

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Fig 3 The value of  $\Phi = \ln \epsilon_{Br}(t_d) + k_{CF_3Br}[CF_3Br]t_d$  as a function of  $[H_2S]t_d$ 

nates which take into account the Br\* quenching by  $CF_3Br$ . From the slope of the plot one may obtain  $k_5 = (6\ 2\ \pm\ 1\ 8) \times 10^{-13} \text{ cm}^3/\text{s}.$ 

The data presented above show that the quenching of I\* and Br\* atoms in the cell may be neglected at  $t_d = 25 \ \mu s$ , when the extent of conversion in reaction (I) is large However the measurements of z at  $t_d = 25 \ \mu s$  have not confirmed the presence of either I\* or Br\* atoms within the limits of experiment accuracy According to eq (3) this gives the estimates  $\epsilon_{Br} < 0.08$  and  $\epsilon_l < 0.15$  (in the latter the uncertainty is larger in view of process (III))

## 4 Discussion and conclusions

The results of the present work are as follows (a) the total rate constant for the H + IBr reaction has some intermediate value between those for reactions (III) and (IV)  $(k_4 = (82 \pm 3.8) \times 10^{-11} [15], 8 \times 10^{-11} [16]$  and  $(6.8 \pm 0.5) \times 10^{-11} \text{ cm}^3/\text{s} [17]$ ), which is inconsistent with the concept of higher reactivity of interhalogens [18]; (b) in reaction (I) the bromine atoms are formed predominantly, i.e. the reaction occurs via the energetically less-favorable reaction path. To explain a similar anomalous branching ratio reported earlier for related reactions H + FCI [2,18,19], H + BrCl [1] and F + ICI [20], some models take into consideration the possibility of atomic migration (in particular of H atoms) within the transition complex [1,2,18,19]

However, analysis of our own and published data

shows all the experimental results are consistent with a simple model of direct H atom reaction with the halogen atom attacked in the (inter)halogen molecule, the probability of this reaction being independent of the identity of any other halogen atom in the molecule

Calculations of potential energy surfaces show that the collinear collisions are most efficient for H atom reactions with (inter)halogen molecules [21]. The large amount of energy released in such reactions and small bond energy in (inter) halogen molecules must results in the short lifetime of the transition complex, and hence in the low probability of its configurational rearrangement Therefore, the collinearly colliding H atom interacts only with the nearest halogen atom and with electrons in a molecular orbital, the energy of which is only slightly dependent on the identity of the other halogen atom Hence, one may assume that H atom reacts with XY molecule just as with  $X_2$ molecule upon collision from the X side, or just as with  $Y_2$  molecule upon collision from the Y side of the interhalogen molecule In other words,

$$k_{XY} = \frac{1}{2}(k_{X_2} + k_{Y_2}), \quad r = \eta_Y / \eta_X = k_{X_2} / k_{Y_2}.$$
 (4)

The validity of this model is confirmed by the reported data for D (H) atomic reactions with  $Cl_2$ ,  $Br_2$ ,  $I_2$ , ICl and IBr in molecular beams [22] the angular distribution of the reaction products is specific for every particular molecule formed, DCl, DBr and DI, but is independent of the identity of the molecule form which they are formed.

The kinetic parameters for the reaction H + IBrand for three other reactions of H and F atoms with interhalogen molecules are collected in table 1 (for F atom reactions with halogen molecules, the same arguments hold true as those for H atom reactions) As is seen, the total rate constants and branching ratios, r, evaluated by using formulae (4) are close to those estimated from the experimental data (though the accuracy of these data is rather poor) The range of validity for this simple model is of interest both for the theory of such chemical reactions and for the quantitative predictions of the rate constants for reactions of H and other atoms with some unstable interhalogens.

The observed absence of noticeable production of I\* and Br\* atoms in the H + IBr reaction is in accord with the experimental data for similar reactions H +

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Table 1

The total rate constants,  $k_{XY}$ , and branching ratios, r, for some reactions  $A + XY \rightarrow AX + Y$ , AY + X determined experimentally and calculated by using formulae (4) from the experimental values of  $k_{X_2}$  and  $k_{Y_2}$ 

			~	-		
 Reaction A + XY	$k_{X_2}^{exp}$ (10 <sup>-11</sup> cm <sup>3</sup> /s)	$k_{Y_2}^{exp}$ (10 <sup>-11</sup> cm <sup>3</sup> /s)	<i>k</i> <sup>exp</sup> XY' (10 <sup>-11</sup> cm <sup>3</sup> /s)	rexp	$k_{XY}^{calc}$ , (10 <sup>-11</sup> cm <sup>3</sup> /s)	rcalc
 H + IBr	30 ± 8 b)	68±82c)	15 ± 4 ª)	4-32 a)	19 ± 4	3-6
H + CIF	25±0.5d)	0 33 ± 0 06 d)	19±03e)	45-621)	14±04	56±10
H + BrCl	6 8-8 2 c)	25±05	-	≥2 5 g)	4 6	2 3 <i>—</i> 4 I
Г + ІСІ	43 ± 11 h)	16 ± 5 h)	50 ± 20 h)	2 7 h)	30 ± 8	1 7-4 9

a) Thus work b) Ref [6] c) Refs [15-17] d) Mean value over all the published data e) kefs [23,24] f) Refs [2,19,25] g) Ref [1] h) Ref [20]

 $Br_2$ , H + HBr [26], H +  $I_2$  [6], and the theoretical concept [25] of a large probability of vibrational excitation of the molecular products in such reactions

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