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Kinetics study of two-channel hydrogen and deuterium atom reactions with interhalogen molecules

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Rate constants and the ratio of rates of two available reaction channels (branching ratios) for the reactions of hydrogen and deuterium atoms with FCl, ICl, and BrF molecules were measured using a fast-flow reactor with RF discharge as source of atoms and with superheterodyne ESR spectrometer as detector. For the reaction with FCl a substantial difference was found in branching ratios when substituting hydrogen atoms with deuterium ones: $\Gamma_{D+FCl}/\Gamma_{H+FCl} = 3.3\pm0.2$. The results are compared with the known experimental data and theoretical calculations; in particular, the possible influence of light atom (H or D) migration in collision complex on reaction mechanism is discussed.

Key words: elementary processes, hydrogen atom reactions, branching, isotopic effect.

Reactions of hydrogen atom with interhalogen molecules (especially with diatomics) are of considerable interest from theoretical and practical points of view. These reactions, accessible for modern theoretical analysis, are of great importance because their studies could illuminate the influence of the dynamics of the elementary act on:

1) ratio of two possible channels rates (branching ratio) k_a/k_b of the reaction

$$H + XY \xrightarrow{k_a} HY + X \qquad (1a)$$

$$\xrightarrow{k_b} HX + Y; \qquad (1b)$$

including the isotopic substitution of H with D (here X and Y are halogen atoms, with X defined to be lighter and more electronegative);

2) populations of internal degrees of freedom (vibrational and rotational) in HX and HY product molecules;

3) effectiveness of the spin-orbital (SO) excitation of X and Y atomic products.

From the practical point of view the reactions under consideration are interesting because a large part of the reaction exothermicity is released into vibrational degrees of freedom with the possibility of inversion like in well-studied reactions

$$H + X_2 \longrightarrow HX + X \qquad (2)$$

Therefore such reactions could be used as chemical laser pumping processes with some principal advantages in comparison with reactions of type (2).

The essential feature of reactions (2) is a significant and monotonic increase in k_2 rate constant values in the X = F, Cl, Br, and I sequence from $3 \cdot 10^{-12}$ cm^3 s^{-1} for F_2 up to $3 \cdot 10^{-10}$ cm^3 s^{-1} for I_2, so the less is both the bond strength of product molecule and the product atom reactivity, the faster is reaction (2) (see Table 1). The low reactivity of heavy halogen atoms observed in

$$X + H_2 \longrightarrow HX + X, \qquad (3)$$

reactions results in a chemical chain process involving reactions (2) and (3) (the greatest advantage of pulsed chemical lasers) being implemented only for H_2+F_2 mixture HF-lasers, *i.e.*, for the chain process with rather slow first step $H+F_2 \rightarrow HF+F$.

The following simple considerations[8] were applied to the description of hydrogen atom reactions (1) as a first approximation: because of collinearity of such processes and because electronic states of any halogen atoms are identical ("resembling" each other), thus it could be assumed that when attacking an XY molecule from the X atom side, the hydrogen atom "feels" it as X_2, and when it attacks an XY molecule from the Y atom side — as Y_2. As a consequence the total rate constant of reaction (1) $k_{XY} = k_a+k_b$ might be represented as $k_{XY} = (k_{X_2}+k_{Y_2})/2$ and the k_a/k_b branching ratio — as k_{X_2}/k_{Y_2}.

It appears that, except for Polanyi's group studies[9—11] there were no systematic studies of the set of the reactions (1). Moreover the data concerned primarily V-R-T distributions in the molecular products . The values of branching ratios were derived from these data using some assumptions and extrapolation and thus are indirect and approximate. Nevertheless the data avail-

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Table 1. Rate constants for H(D) + X_2 reactions and dissociation energies of reagent and product molecules

$L+X_2$	$k_{X_2}/cm^3\ s^{-1}$	References	D_{X_2}/ kcal mol^{-1}	D_{LX}/ kcal mol^{-1}
$H+F_2$	$(3.3\pm0.6)\cdot10^{-12}$	*	37.0	35.3
$D+F_2$	$(2.3\pm0.4)\cdot10^{-12}$	*	37.0	136.6
$H + Cl_2$	$(1.94\pm0.25)\cdot10^{-11}$	1	57.2	102.2
	$(2.19\pm0.32)\cdot10^{-11}$	2		
	$(2.13\pm0.78)\cdot10^{-11}$	3		
	$(1.70\pm0.26)\cdot10^{-11}$	4		
	$(1.83\pm0.12)\cdot10^{-11}$	**		
$D + Cl_2$	$(1.4\pm0.3)\cdot10^{-11}$	*	57.2	103.4
$H + Br_2$	$(8.2\pm3.8)\cdot10^{-11}$	3	45.4	86.6
	$(6.6\pm0.4)\cdot10^{-11}$	5		
	$6.15\cdot10^{-11}$	6		
	$(7.3\pm0.9)\cdot10^{-11}$	**		
$D + Br_2$	$(5.1\pm0.7)\cdot10^{-11}$	*	45.4	87.8
$H + I_2$	$(3.0\pm0.8)\cdot10^{-10}$	7	35.6	70.4
$D + I_2$	$(2.1\pm0.6)\cdot10^{-10}$	*	35.6	71.4

* "Mean" value for all data known to us.

** This work.

able until recently[9—12] do not contradict the simple model mentioned above. However the accuracy of the experimental data available is far from the desirable level, and for the H atom reactions with XY molecules, when X and Y atoms are not "neighbors" in the VIIth column of periodic table (when the highest k_a/k_b ratios could be expected), quantitative data is practically absent. The latter stands also for the whole D atom set of the reactions (1) because of the lack of sensitivity of IR chemiluminescence technique used[13,14] (DX molecules are much less emissive then their HX analogs).

Theoretical trajectory calculations are available for H+ICl[15,16] and H+BrCl[17] reactions. They clearly point to the significance of light H atom migration from a light halogen atom to heavy one in the collisional complex.

The existence of migration and its mechanism for the reactions examined were proposed by Polanyi and coworkers on the background of their observation of the bimodalities of the rotational distributions (*J*) for light molecular products[11]. They attributed the appearance of these bimodalities to the two possible routes of HX product molecules formation in the elementary process: the direct route led to the product with low rotational quantum numbers *J*, and the migrational one yielded molecules with high *J*.

To ascertain the real features of the dynamics of elementary act between hydrogen and interhalogenides as well as prospects for development of effective halogen hydride chain chemical lasers, further kinetic studies are an extreme necessity. And it would be advantageous to use a technique alternative to the IR-chemiluminescence method used by Polanyi's[13] and Setser's[14] groups, which detected only HX and, in principle, HY molecules.

The technique proposed is electron spin resonance (ESR), which we used in this work with the discharge-flow reactor. Obviously, under flow conditions, all detailed information concerning V-R and angle distributions (accessible in molecular beam studies) is lost. But it is possible to detect both the reagent (H(D)) and the product (X and Y) atoms and thus to measure indirectly the branching ratios and rate constants. As will be discussed below, the branching ratio values can give very valuable information, as they are greatly influenced by the transition complex dynamics.

We especially emphasize the advantages of ESR to study reactions of deuterium atom and bromine- and iodine-containing molecules, when low probabilities of IR emission transitions make the chemiluminescent method inappropriate.

Experimental

We used a home-built superheterodyne ESR spectrometer with a flow reactor[18] used in our previous studies of gas-phase processes involving $Br(^2P_{1/2})$ atoms[19,20]. The technique was described in detail elsewhere[18]. The flow reactor was manufactured from a quartz tube passed through a microwave ESR cavity (H_{011} mode). Atomic reagents were formed from the parent molecular species in the RF capacitance discharge. Molecular reagents were injected below the discharge through a thin quartz capillary along the reactor axis. The distance x between the injection point and the detection zone (*i.e.*, the cavity center) was varied by moving the reactor relative to the cavity.

To reduce the influence of heterogeneous processes and to increase the concentration sensitivity of the spectrometer, we increased the gas conductivity of the flow reactor. New reactor was made of a thin-wall (0.5 mm) quartz tube with 1.7-cm inner diameter. The larger diameter of the reactor as compared to one of our previous studies[18—20] resulted in a 2.5-times increase in the buffer gas flow with the same pressure, or with the same buffer flow its pressure could be decreased by the same factor, which is equivalent to the increase of the spectrometer sensitivity when working with collisionally broadened lines.

We succeeded in achieving a magnetic field stability of at least 70 mOe within 5 minutes time interval for a magnetic field region from 2 to 10 kOe. This allowed a long-time (at least 10 minutes) acquisition of narrow ESR signals without any additional magnetic field correction.

The cylindrical microwave cavity was composed of six silvered brass rings, isolated from each other and connected by epoxy glue. It was 25 mm in length and 47 mm in diameter, with a diameter of the holes in its faces of 19 mm. The quality factor of the cavity was determined to be about 10^4.

The set measures undertaken made it possible to increase significantly the sensitivity of the spectrometer and to observe excited halogen atoms in concentrations useful for kinetic studies — $10^{11}\div10^{13}$ cm^{-3}.

Table 2. The values of branching ratios and rate constants for H(D) + XY reactions (experimental data and the values obtained with a simple model)

L+XY	Γ	References	k_{Y_2}/k_{X_2}	$k_{XY}/cm^3\ s^{-1}$	References	$(k_{X_2}+k_{Y_2})/2/cm^3\ s^{-1}$
H+FCl	6.7±0.8	10	5.8			$1.1 \cdot 10^{-11}$
	5.2±0.5	12		$4.1 \cdot 10^{-11}$	12	
	6.1	23		$(3.7\pm0.4) \cdot 10^{-11}$	**	
	2.5±0.2	*		$(4.04\pm0.25) \cdot 10^{-11}$	*	
D+FCl	8.5±0.5	*	6.1	$(3.14\pm0.20) \cdot 10^{-11}$	*	$3.8 \cdot 10^{-11}$
H+FBr	≥(5–24)	11	22.0			$3.7 \cdot 10^{-11}$
	0.38±0.06	*		$(2.9\pm0.7) \cdot 10^{-11}$	*	
D+FBr	0.38	*	22.0	$(1.9\pm0.4) \cdot 10^{-11}$	*	$2.7 \cdot 10^{-11}$
H+ClBr	2.5±0.3	9	3.7			$4.5 \cdot 10^{-11}$
D+ClBr			3.6			$3.3 \cdot 10^{-11}$
H+ClI	<0.5	24	15.8	$4.9 \cdot 10^{-11}$	12	$1.6 \cdot 10^{-10}$
				$(5\pm2) \cdot 10^{-11}$	27	
	0.65±0.10	*		$(1.21\pm0.09) \cdot 10^{-10}$	*	
D+ClI	0.65	*	15.0	$(9.69\pm0.12) \cdot 10^{-11}$	*	$1.1 \cdot 10^{-10}$
H+BrI	≈0.3	25	4.2			$1.9 \cdot 10^{-10}$
	(4—32)	8		$(1.5\pm0.4) \cdot 10^{-10}$	8	
D+BrI			4.1			$1.3 \cdot 10^{-10}$

* This work. ** Rate constant[26] for HCl+F reaction.

Absolute atomic concentrations were determined by a method[21] based on calibration by molecular oxygen.

The values of reaction branching ratios were determined by extrapolation of the measured [X]/[Y] ratio dependence on x to $x = 0$. The values obtained are listed in Table 2 together with those known from the literature.

The rate constants were measured under conditions when the reactions under study could be confidently considered as pseudo-first-order. Thus the absolute rate constant value was determined as a slope of $(v_{mean}/N_0) \cdot \ln(n/n_0)$ dependence vs. x, where N_0 is the initial concentration of molecular reagent, v_{mean} is the mean flow velocity, and n is the hydrogen (deuterium) concentration. Thus, the resulting values of rate constants are listed in Table 2, and necessary details of particular rate constant measurements are discussed in the corresponding sections below.

We used FCl, ICl and FBr as reagents. Chlorine monofluoride (FCl) was prepared by a method[22] in which an F_2 and Cl_2 stoichiometric mixture was burnt in a stainless steel vessel by electric spark ignition. Each portion obtained was frozen in a separate volume. The gas collected was purified by multiple pump-and-freeze cycles.

Iodine monochloride (ICl) was obtained by direct chlorination of solid iodine by chlorine gas in a quartz vessel. It was also purified by multiple pump-and-freeze cycles.

Bromine monofluoride (FBr), which does not exist in a stable state, was produced steadily in experiments by a technique that will be described below in the corresponding section.

Typical conditions of the discharge-flow experiments were: Ar buffer gas pressure from 0.7 to 3.3 Torr, flow velocity from 27 to 49 m s^{-1}, and hydrogen atom concentration from $1 \cdot 10^{12}$ to $3 \cdot 10^{13}$ cm^{-3}.

Results and Discussion

Reaction

$$H(D) + FCl \longrightarrow HCl(DCl) + F,\ HF(DF) + Cl \qquad (4)$$

This reaction is the most well studied until now. Note it is also the slowest among the reactions under consideration, and thus the experimental data obtained could be strongly affected by a F+HCl secondary process which presumably can proceed with a gas-kinetic rate constant in the case of a vibrationally excited HCl product[13] of primary reaction (4). So in our studies we paid special attention to reaction (4).

Figure 1 shows the experimental data on reaction (4), namely the dependence of Cl and F product atoms concentrations and also their ratio [F]/[Cl] on distance x. Growth of concentrations is caused by reaction (4), while their decrease naturally can be related to the secondary process

$$F + HCl(v) \longrightarrow HF(v) + Cl, \qquad (5)$$

Indeed, the reaction (5) rate constant k_5 $8 \cdot 10^{-11}$ $cm^3\ s^{-1}$, estimated from the experimental data is much larger than that known from literature $k_5 = (1.6\pm0.6) \cdot 10^{-11}$ $cm^3\ s^{-1}$ [29]. This demonstrates the well

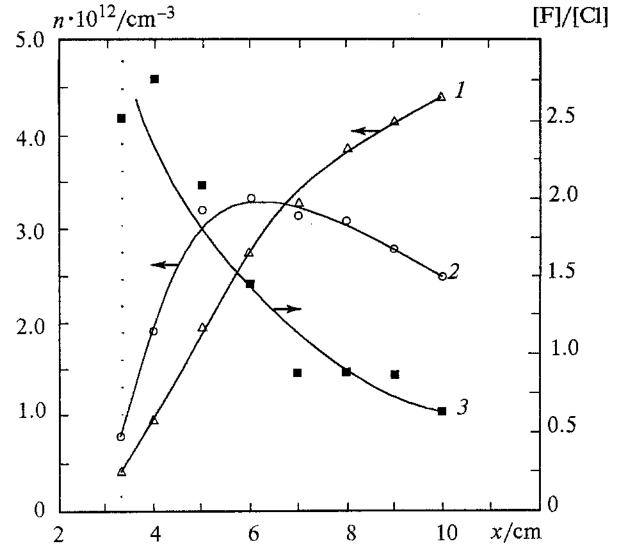

Fig. 1. Experimental dependencies of [Cl] (*1*), [F] (*2*), and Γ (*3*) on *x* for H+FCl reaction. v_{mean} =27 m c^{-1}, p_{Ar}=0.7 Torr (in this Figure and other Figures the dot line indicates the point of injection of a molecular reagent; the curves are drawn for illustration).

known fact that the reaction (5) is accelerated by vibrational excitation of the HCl reagent.

The [F]/[Cl] ratio extrapolated to the reagents mixing point (see Fig.1) gives us the value of the reaction (4) branching ratio Γ_4 k_4^{F}/k_4^{Cl} = 2.5. This value confirms the known fact that the channel of formation of F atoms is prevalent, but the branching ratio itself is noticeably smaller than the experimental values obtained by chemiluminescent methods Γ_4 = 6.7[10], 5.2[12], 6.1[23] as well as that predicted by the "simple" model mentioned in the Section 1.

One could explain the discrepancy observed by a partial conversion of F atoms into Cl ones *via* reaction (5) assuming it is fast enough to have time to proceed in the zone of reagent mixing. However to achieve quantitative agreement it is necessary to assume that with 1/3 of HCl molecules just produced in (4), reaction (5) proceeds with a rate constant of about $3 \cdot 10^{-10}$ $\text{cm}^3\ \text{s}^{-1}$.

To refine the Γ_4 value we used the following modification of the method of competitive reactions. It is well known that the F atoms react with CH_4 with a rate constant three orders of magnitude larger than that of Cl+CH_4 (reaction k_{F+CH_4} = $7.5 \cdot 10^{-11}$ $\text{cm}^3\ \text{s}^{-1}$ [29], k_{Cl+CH_4} = $8 \cdot 10^{-14}$ $\text{cm}^3\ \text{s}^{-1}$ [30]), and CH_3 radicals produced in these reactions are much less reactive than hydrogen and halogen atoms. In these experiments we injected methane between the RF discharge zone and the FCl injection zone. The CH_4 flow rate was chosen to cause a slight [Cl] decrease with a long time for reagent contact τ_c. Obviously, the fluorine atoms, ESR signal was not detected in such experiments. Since the F+CH_4 reaction rate was much greater than any expected for F+HCl(v) one, so the conversion of fluorine atoms into chlorine ones was eliminated. Comparison of the dependence of *x* [Cl] (in the absence of CH_4) and $[Cl]_{CH_4}$ (in the presence of CH_4) shown in Fig. 2 confirms that there were no sources of Cl atoms in the system at low τ_c except the second channel of (4): it is seen that $[Cl]/[Cl]_{CH_4} \to 1$ when $x \to 0$. Note that the $([F]+[Cl])\ /[Cl]_{CH_4}$ value must be equal to Γ_4+1 when x = 0 (at this point the influence of heterogeneous processes is negligible). The branching ratio thus obtained $\Gamma_4 = 2.5 \pm 0.2$ coincides with that measured directly (see above).

The relatively low value of Γ_4 indicates the important role of the H atom migration from the heavier Cl atom

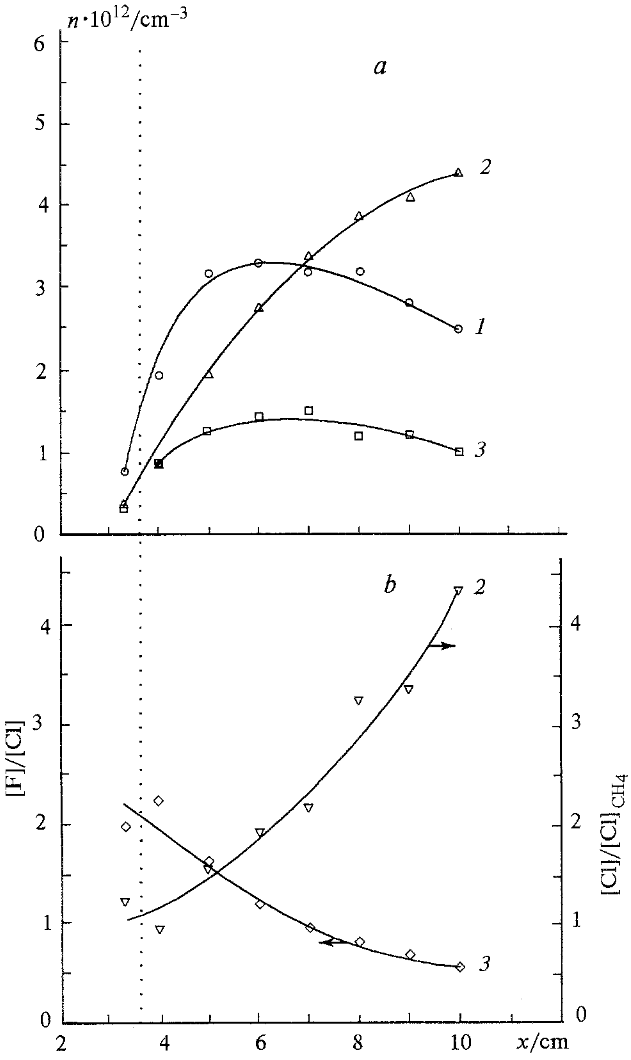

Fig. 2. Atomic concentrations (*a*) and their ratios (*b*) for the determination of branching ratios in H+FCl reaction using CH_4: $[FCl]_0$ = $1.1 \cdot 10^{14}$ cm^{-3}, $[CH_4]$ = $2.3 \cdot 10^{15}$ cm^{-3}, v_{mean} = 27 m s^{-1}, p_{Ar} = 0.7 Torr; *1*, [F]; *2*, [Cl]; *3*, $[Cl]_{CH_4}$.

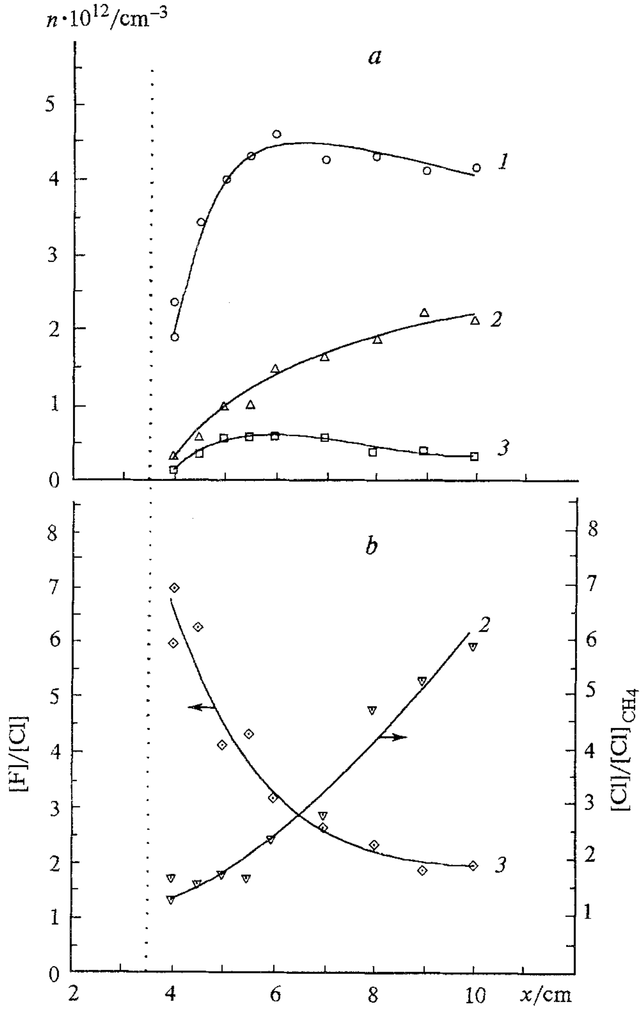

Fig. 3. Atomic concentrations (*a*) and their ratios (*b*) for determination of branching ratios in H+FCl reaction using CH_4 Explanations see Fig. 2.

to the lighter F atom in the transition complex, and simultaneously points to the possibility of a significant effect of isotopic substitution on the reaction (4) branching ratio. In our experiments substitution of D for H indeed turned out to increase the Γ_4 value up to 6.7. But the real Γ^D_4 value must be even larger, because there were traces of water in the Ar buffer gas, which results in the small amount of the "background" hydrogen atoms in the RF discharge products. This amount was measured by ESR to be about $1 \cdot 10^{12}$ cm^{-3} in the absence of H_2 in the discharge, and it evidently has no effect on the studies of the H atom reactions. But simple calculation taking into account the effect of this H atoms concentration on the D atoms reaction along with $\Gamma^H_4 = 2.5$ gave us $\Gamma^D_4 = 9$ at $[D]_0 = 3 \cdot 10^{12}$ cm^{-3}. Taking into account this estimate, we carried out the measurements with an argon pipeline cooled by vapors of liquid nitrogen. Thus we diminished [H] to the amount of $2 \cdot 10^{11}$ cm^{-3} so it had no effect on the experimental results anymore. The data shown in Fig. 3 led to the $\Gamma^D_4 = 8.5 \pm 0.5$ value, being in good agreement with the above estimate and resulted in the value of branching ratio isotopic effect $\Gamma^D{}_4/\Gamma^H{}_4 = 3.3$ which seems to be unusually high for such a "simple" atom-diatom reaction.

We also measured the absolute rate constants of reaction (4) and (as a test of reliability)

$$H + Cl_2 \longrightarrow HCl + Cl \qquad (6)$$

under the conditions when reactions could be considered confidently as pseudo-first-order ones (see Fig. 4 and the data in its caption). A least mean squares processing of the Fig. 4 data gave the values of k_4 and k_6 shown in Tables 2 and 1, respectively. Note the very good agreement of the k_6 value obtained with those from literature cited in Table 1. The $k^H{}_4 = (4.04 \pm 0.12) \cdot 10^{-11}$ cm^3 s^{-1} and k_4/k_6 values are also in agreement with the results of Setser *et al.*[12]. Note also the $k^H{}_4$ value is three times greater than the value predicted by the "simple" model.

$$H(D) + ICl \longrightarrow HI(DI) + F, HCl(DCl) + I \qquad (7)$$

This of interest because the ICl molecules consist of two atoms noticeably different in mass and size (Cl and I atoms are not neighbors in the periodic table). Along

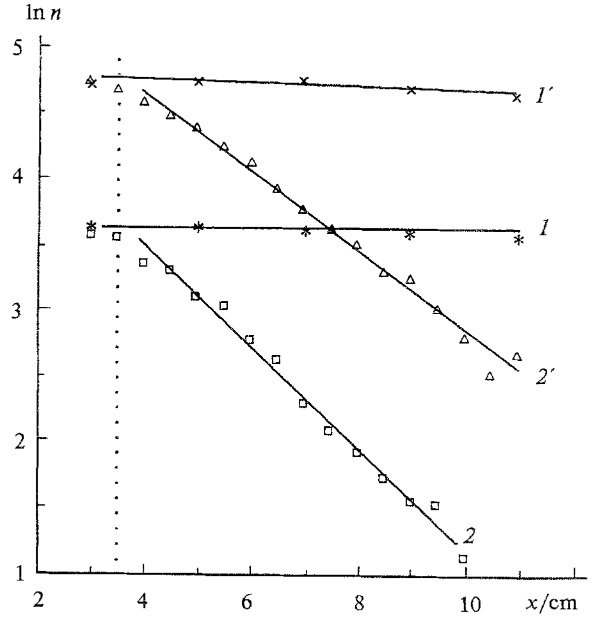

Fig. 4. Experimental dependencies for the determination of rate constants for H(D) + FCl reactions: $v_{mean} = 43$ м · с$^{-1}$, p_{Ar} = 1.7 Torr, $[H]_0 = 1.8 \cdot 10^{12}$ cm^{-3}, $[D]_0 = 2.2 \cdot 10^{12}$ cm^{-3}, $I_{FCl} = 4 \cdot 10^{17}$ s^{-1}, $I_{Ar} = 5.3 \cdot 10^{20}$ s^{-1}; *1*(*1'*), [H]([D]) without FCl; *2*(*2'*), [H]([D]) with $[FCl]_0 = 4.1 \cdot 10^{13}$ cm^{-3}. Dependencies of [H] are shifted downwards for a unit.

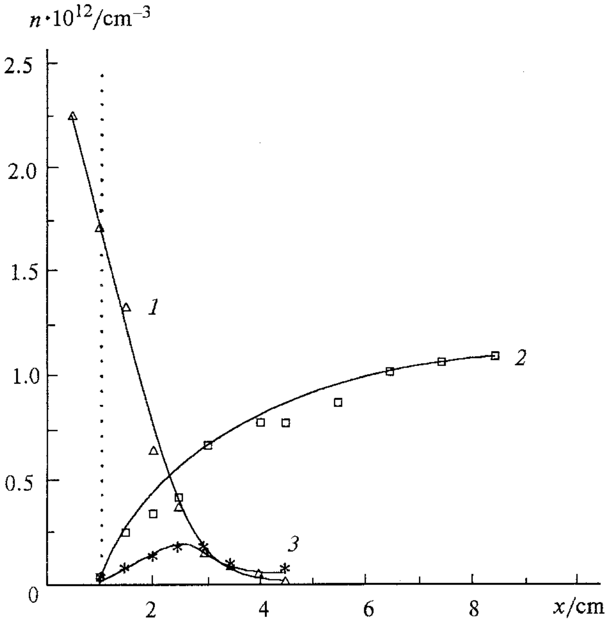

Fig. 5. Atomic concentrations for H+ICl reaction: v_{mean} = 27 m s^{-1}, p_{Ar} = 0.7 Torr, $[\text{H}]_0$ = $2.2 \cdot 10^{13}$ cm^{-3}, $[\text{ICl}]_0$ = $3.3 \cdot 10^{12}$ cm^{-3}, I_{Ar} = $1.4 \cdot 10^{20}$ s^{-1}; *1*, [H]; *2*, [I]; *3*, [Cl].

with the Polanyi group's experimental results on this reaction mentioned in Section 1 (see Table 2), there are two trajectory calculations that gave different branching ratio values (Γ_7 = 0.3 [15] and Γ_7 = 0.75 [16]) but both pointed to the importance of the H atom migration in the transition complex: in the absence of migration the "simple" model[8] gives Γ_7 = 14.

Experimental dependencies of H, I, and Cl atom concentrations on *x* are shown in Fig. 5. A [Cl] decrease at large x is due to a secondary reaction

$$\text{Cl} + \text{HI} \longrightarrow \text{HCl} + \text{I}, \qquad (8)$$

which could be accelerated *via* vibrational excitation of HI, the reaction (7) product.[31]

To make sure the reaction (8) effect on the measured reaction (7) branching ratio is negligible, we measured the [Cl]/[I] ratio at a fixed distance x = 1 cm (small τ_c, see Fig. 5) at various initial concentrations of the hydrogen atoms. Results are shown in Fig. 6 as the [Cl]/[I] ratio dependence on the measured hydrogen atom concentration. An extrapolation of the branching ratio to [H] = 0 gives the value of Γ_7 = 0.65 ± 0.10. Note the weak [Cl]/[I] dependence on [H], which allows us to assert that with small time for reagent contact, the reaction (8) effect is negligible.

The experimental value of Γ_7 when D atoms were substituted for H ones appeared to be equal to that for H atoms, reaction (see Table 2).

Absolute rate constants of H+ICl and D+ICl reactions were measured as described above. The $\ln([\text{H}]/[\text{H}]_0)$ and $\ln([\text{D}]/[\text{D}]_0)$ dependencies are shown in Fig. 7. Mean least squares processing of these data results in the reaction (7) rate constant shown in Table 2 and $k^{\text{H}}{}_7/k^{\text{D}}{}_7$ = 1.3±0.1.

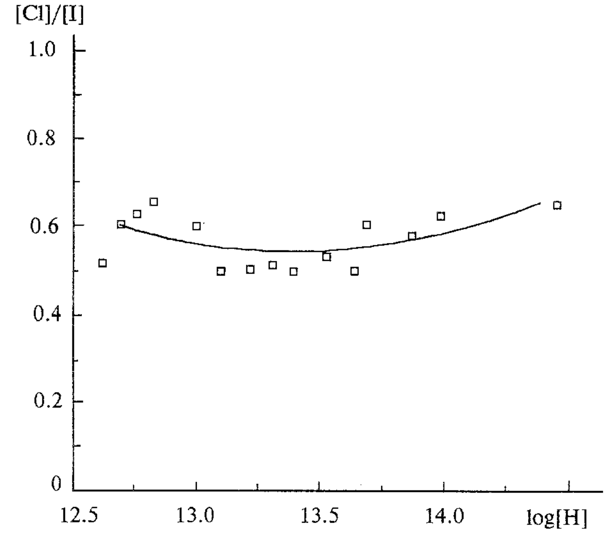

Fig. 6. Dependence of the branching ratios in H+ICl reaction on $[\text{H}_0]$: v_{mean} = 27 m s^{-1}, p_{Ar} = 2.7 Torr, τ_c = 0.37 ms (x = 1 cm).

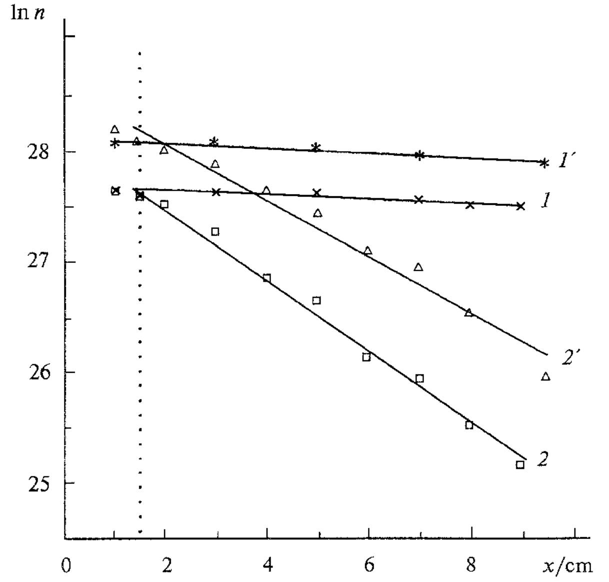

Fig. 7. Experimental dependencies for determination of rate constants for H(D)+ICl reactions: v_{mean} = 43 m s^{-1}, p_{Ar} = 1.7 Torr, $[\text{H}]_0$ = 10^{12} cm^{-3}, $[\text{D}]_0$ = $1.6 \cdot 10^{12}$ cm^{-3}; *1*(*1′*), [H]([D]) without ICl; *2*(*2′*), [H]([D]) with $[\text{ICl}]_0$ = $1.1 \cdot 10^{13}$ cm^{-3}.

Reaction

$$\text{H(D)+BrF} \rightarrow \text{HF(DF)+Br, HBr(DBr)+F} \qquad (9)$$

The BrF molecule does not exist at room temperature at stationary conditions because the equilibrium $3\text{BrF} \rightleftarrows \text{Br}_2\text{+BrF}_3$ is shifted to the right side at room temperature. Therefore we had to use an on-stream BrF production implemented by the following procedure. A near stoichiometric mixture of Br_2 and F_2 was injected into a 2-mm internal diameter 30-cm long nickel capillary connected to a thin quartz capillary to inject products into the flow reactor. The nickel capillary was heated up to 700 °C by passing an electric current through it, and the mixture pressure on its entrance was a few Torr. A thermodynamic calculation showed that there were almost entirely BrF molecules in the gas under such conditions.

It was critical to ensure the absence of Br_2 molecules in the products injected into the flow reactor. The absence of Br_2 was tested in the following experiment. It is well known that F atoms react with Br_2 with a large rate constant $k = (2.2\pm1.1)\cdot10^{-10}$ cm^3 s^{-1} [32], and do not react with BrF. Therefore before the kinetic measurements, F_2 was injected instead of H_2 into the discharge flow to generate fluorine atoms. Their ESR signal was essentially constant along the flow reactor in the absence of Br_2 and F_2 in the nickel capillary. After that Br_2 and F_2 flows injected into the heated capillary were adjusted to ensure not more than a 20 % decrease in the F atoms ESR signal in all measurement zones downstream of the injection point; this corresponded to a residual Br_2 concentration less than $1\cdot10^{12}$ cm^{-3} when the initial BrF concentration $[BrF]_0 = 7\cdot10^{13}$ cm^{-3} (see Fig. 8 caption). A simple calculation showed that with Br_2 and F_2 flows used in our experiments, the maximum possible concentrations of BrF_3 and BrF_5 were not more than $0.1[BrF]_0$ and $0.02[BrF]_0$, respectively.

Experimental data on the branching ratio and reaction (9) rate constant measurements are shown in Fig. 8 and Fig. 9, respectively. To determine the k_9 absolute value more reliably, we also measured the H atoms' decay kinetics with the F_2 flow turned off, *i.e.*, *via* a $H+Br_2$ reaction. Because in the measurements of the rate constant we had $[H]_0<<[BrF]_0$, $[Br_2]_0$ (see Fig. 9) and in the absence of molecular reagents we did not observe any remarkable heterogeneous loss of H atoms, we considered reaction (9) kinetics as pseudo-first-order.

The least mean squares processing of Fig. 9 dependencies resulted in the values of $k^{H}_9 = (2.9\pm0.7)\cdot10^{-11}$ cm^3 s^{-1} and $k_{H+Br_2} = (7.3\pm0.9)\cdot10^{-11}$ cm^3 s^{-1} (errors indicated are two standard deviations, *i.e.*, ±2). It is seen from Table 1 that the k_{H+Br_2} value agrees very well with the published data. The k^{H}_9 error value is rather large (25 %) because the $[BrF]_0$ was monitored by an indirect procedure with precision not better than 20 %.

As seen from Fig. 8 the reaction (9) main channel is that resulting in the formation of Br and HF. The value of the branching ratio $\Gamma^{H}_9 = 0.38\pm0.06$ was determined from the Fig. 8 data as a mean value of the [F]/[Br] ratio over six data points (*i.e.*, at $x \leq 3$ cm). In contrast to the H+FCl reaction, here the channel producing heavy Br atoms appeared to be prevalent, so the effect of the secondary F+HBr reaction (k =

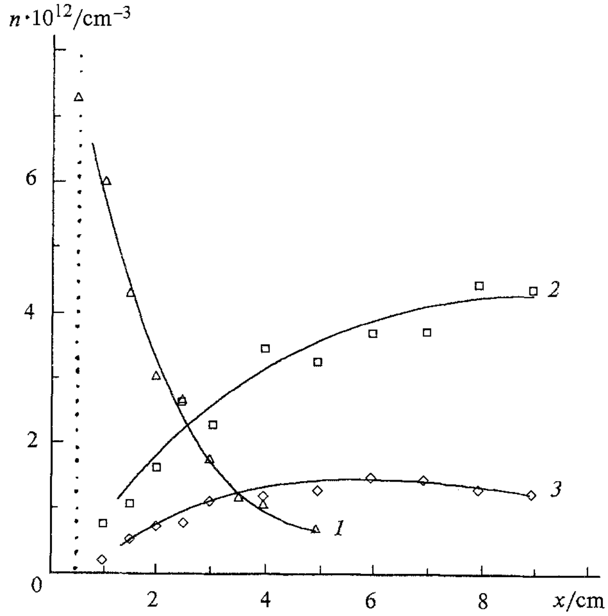

Fig. 8. Atomic concentrations for H+FBr reaction: v_{mean} = 38 m s^{-1}, p_{Ar} = 1.1 Torr, $[H]_0 = 7.2\cdot10^{12}$ cm^{-3}, $[FBr]_0 = 7\cdot10^{13}$ cm^{-3}, $I_{Ar} = 3.3\cdot10^{21}$ s^{-1}, $I_{Br_2} = 3\cdot10^{17}$ s^{-1}, $I_{F_2} = 4.1\cdot10^{17}$ s^{-1}; *1*, [H]; *2*, [Br], *3*, [F].

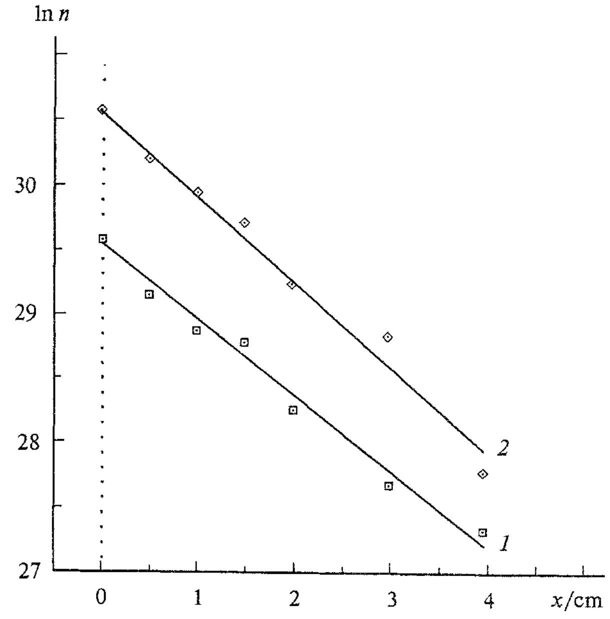

Fig. 9. Dependencies of [H] on x for H+FBr and $H+Br_2$ reactions: v_{mean} = 38 m s^{-1}, p_{Ar} = 1.1 Torr, $[H] = 7.2\cdot10^{12}$ cm^{-3}, $[Br_2]_0 = 3.5\cdot10^{13}$ cm^{-3}, $[FBr]_0 = 7\cdot10^{13}$ cm^{-3}, $I_{Ar} = 1.15\cdot10^{21}$ s^{-1}, $I_{Br_2} = 3\cdot10^{17}$ s^{-1}, $I_{F_2} = 4.1\cdot10^{17}$ s^{-1}; *1*, H + BrF; *2*, H + Br_2.

$3 \cdot 10^{-11}$ cm^3 s^{-1} [33]) should be negligible, as was mentioned in the previous Section, and our calculations of the reaction (9) kinetics confirmed that this was true for $x < 5$ cm.

Under the same experimental conditions we measured branching ratio and rate constant values for the D+BrF reaction. The $\Gamma^D{}_9$ value obtained appeared to be the same as for H atoms' reaction, and k_H+BrF/k_D+BrF = 1.5, *i.e.*, there is no significant difference in H and D atom reactions cross sections.

An analysis of the results presented above, along with the other experimental and theoretical results (for a summary see Tables 1 and 2) allowed us to draw at least two conclusions. First, there exists the appreciable probability of light H(D) atom migration in the transition complex and therefore the channel rates ratio value differs noticeably from that resulting from the simple model. Second, reactivity of the interhalogen molecule is specified by its heaviest atom so that the total reaction rate constant appears to be close to that for the reaction with the corresponding symmetric molecule.

Note that the possibility of migratory paths was also indicated in the studies of fluorine atom reactions with halogen and interhalogen molecules (I_2[34], ICl [35]).

To our knowledge, a general picture of the light atom migration route during the reaction time has not been described theoretically so far. But from the classical calculations (somewhat illustrative) one can learn at least two crucial features about it: first, migration means the existence of a state with a "long" lifetime as compared to the time-of-flight; second, migration "converts" a L+H—H (Light+Heavy-Heavy) configuration to a H—L—H one, *i.e.*, to the light-atom-transfer reaction in which quantum effects must be accounted for. In turn, these features could be generalized as the existence of some quasi-bound state(s) in the collision complex. Such "long-lived" states are very well known in nuclear physics and usually are associated with resonance or virtual states and threshold effects[36,37]. In atom-molecule reactive collisions, quasi-bound or resonance states were revealed experimentally for the first time in the molecular-beam study of the $F+H_2(D_2)$ reaction[38]. Experimental and theoretical studies[39] of photoelectron spectroscopy of XHY^- complexes also showed the existence of resonant states in the XHY transition complex, as did the study of the $H+H_2$ exchange reaction[40].

In general, quasi-bound states cannot manifest themselves in the integral cross sections (rate constants in our case). But they can greatly influence different channels' ratios[37]. We suppose that the large isotopic effect for the H+FCl reaction branching ratio observed in the present study is the manifestation of the influence of such states on the dynamics of the HFCl transition complex.

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