

# Abstraction fraction in the reaction of deuterium atoms with HBr and HI \*

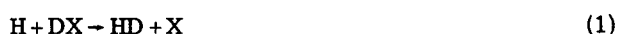
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The reaction between D atoms and HX molecules (X=Br or I) may result in either abstraction of H atoms to yield HD+X or exchange of H atoms to yield DX+H. This reaction was studied at 300°K by photolyzing HX+DX+He mixtures with monochromatic light at two wavelengths. It was found that the abstraction fraction is  $0.76 \pm 0.10$  for X=Br and  $0.88 \pm 0.08$  for X=I. These results are discussed in terms of the dynamics of these reactions.

## I. INTRODUCTION

In previous work done in this laboratory<sup>1</sup> the competition between the reactions



and



where the halogen X was either Br or I, was studied. Values were reported for the abstraction fraction defined by

$$a(\text{H} + \text{DX}) = k_1 / (k_1 + k_2), \quad (3)$$

where  $k_1$  and  $k_2$  are the thermal rate constants of Reactions (1) and (2), respectively.  $a(\text{H} + \text{DX})$  was determined from experiments in which HX+DX+He mixtures were photolyzed with monochromatic light at several wavelengths.

The  $[\text{HX}]/[\text{DX}]$  ratio in those experiments was of the order of a few percent. The method used was based on the strong dependence of the extinction coefficient ratio  $\epsilon_{\text{HX}}/\epsilon_{\text{DX}}$ —and therefore of the ratio of the amounts of H and D atoms formed by photodissociation—on the wavelength of the photolyzing light. These atoms were partly thermalized by collisions with helium before they reacted with HX or DX. By extrapolating the experimental results to conditions of complete thermalization ( $[\text{DX}]/[\text{He}] \rightarrow 0$ , a value for  $a(\text{H} + \text{DX})$  for thermal H atoms was obtained.

In the present paper we describe the use of an analogous technique to determine the abstraction fraction in the reaction of D atoms with HX molecules. This fraction is defined similarly by

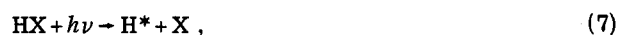
$$a(\text{D} + \text{HX}) = k_5 / (k_5 + k_6), \quad (4)$$

where  $k_5$  and  $k_6$  are, respectively, the rate constants for the reactions



We photolyzed HX+DX+He mixtures, under conditions such that the hot H and D atoms are almost completely thermalized by collisions with helium atoms before reacting with HX or DX. For conditions under which the conversion of the hydrogen halides is small and the thermalization of the H and D by He is complete, the perti-

nent reaction mechanism is



From this mechanism we get the steady state expression

$$\frac{[\text{D}]}{[\text{H}]} = \beta \frac{Y[k_{12} + \beta(k_1 + k_2)] + k_2}{k_{11}\beta + k_5 + k_6 + k_8\beta Y}, \quad (14)$$

where

$$Y = \epsilon_{\text{DX}}/\epsilon_{\text{HX}}$$

and

$$\beta = [\text{DX}]/[\text{HX}].$$

The corresponding reaction product ratio is given by

$$\left(\frac{[\text{HD}]}{[\text{H}_2]}\right)_0 = M + \beta Y \frac{1 + M(1 + \beta k_{11}/k_5) - \beta^2 r(k_{11}/k_5)^2}{1 + \beta(k_{11}/k_5) + (1 + Y\beta)k_6/k_5}, \quad (15)$$

where

$$M = r \frac{k_{11}}{k_5} \beta \left(1 + \frac{k_2/k_1}{\beta k_{11}/k_5 + 1 + k_6/k_5}\right), \quad (16)$$

$$r = \frac{k_1/k_{12}}{k_{11}/k_5}, \quad (17)$$

and the subscript zero in  $([\text{HD}]/[\text{H}_2])_0$  indicates that the limit  $([\text{HX}]/[\text{He}]) \rightarrow 0$  has been taken.

Two important differences exist between the conditions of the present experiments and those of Ref. 1. In the latter, the  $[\text{HX}]/[\text{DX}]$  ratios used, ranging from 0.02 to 0.06, were sufficiently small to permit the neglect of Reaction (12). In the present experiments, a careful analysis of Eq. (15) indicates that relatively large  $\beta = [\text{DX}]/[\text{HX}]$  values (about 0.24) had to be used to com-

pensate for the smallness of the values of  $Y = \epsilon_{DX}/\epsilon_{HX}$  listed in Table I and still produce appreciable changes of  $([HD]/[H_2])_0$  with changes in the wavelength of the photolyzing light. As a result, Reaction (11) cannot be excluded from the mechanism. The second difference is that in the H+DX experiments of Ref. 1, the isotopic impurity HX in the DX used was not known to high accuracy and depended on the degree of deuteration of the walls of the vacuum system in which it was handled. As a result, the  $[HX]/[DX]$  ratio had to be determined as part of the experiment. In the present D+HX studies, the HX impurity in the DX did not significantly affect the large  $[DX]/[HX]$  ratios used. These could be accurately determined from the known amounts of pure HX and impure DX employed in the preparation of the HX+DX mixtures plus an approximate knowledge of the isotopic impurity of the DX.

As a result of these differences, the details of the handling of the data in the present study, based on Eqs. (15)–(17), differ from Ref. 1. In Sec. II we summarize the experimental procedure, in Sec. III we describe the data processing and give the results which we discuss in Sec. IV.

## II. EXPERIMENTAL PROCEDURE

DBr (98% stated isotopic purity) and DI (99% stated isotopic purity) were supplied by Merck, Sharp and Dohme of Canada, Ltd. HI and HBr (over 99% chemical purity) were supplied by the Matheson Company and purified by trap-to-trap distillation. Helium of ultrahigh purity (exceeding 99.99%) was also supplied by Matheson.

HX+DX mixtures were accurately prepared in a 1-liter flask painted black externally. Pressures were measured with a Pace Model P7D pressure transducer, which was used as a null indicator, with a mercury manometer as reference. The  $[DX]/[HX]$  ratio was  $0.239_6 \pm 0.001$  for the HBr + DBr mixture and  $0.234_4 \pm 0.001$  for the DI + HI mixture.

The experimental procedure was similar to that described in Ref. 1. DX+HX+He mixtures, with accurately measured  $([HX]+[DX])/[He]$  ratios, were prepared in a cylindrical quartz reaction cell (140 mm long and 40 mm in diameter) with optically flat quartz windows at its ends and photolyzed with monochromatic light at a certain wavelength. After photolysis at room temperature the reaction cell was immersed in liquid nitrogen

for about 20 min. The uncondensed gases (He, H<sub>2</sub>, HD, and D<sub>2</sub>) were transferred with the aid of a toepler pump, through a trap cooled with liquid nitrogen, to a sample tube. The  $[H_2]/[HD]$  ratios were then determined with a CEC 21-103 C mass spectrometer. H<sub>2</sub> plus HD mixtures of accurately known composition were used for the calibration of the mass spectrometer.

At each wavelength  $\lambda$  used experiments were carried out with 12–18 mixtures having different  $([HX]+[DX])/[He]$  ratios, usually in the range 0.08–0.8. Pressures in the reaction cell were in the range 50–250 torr. Photolysis time was between 20 min and 7 h, depending on the wavelength used and the composition of the reaction mixture. The conversion of hydrogen halide during photolysis was usually lower than 1.5%.

The light sources employed were: (a) for  $\lambda = 2138 \text{ \AA}$ , a zinc Phillips spectral lamp with *cis*-2-butene gas filter; (b) for  $\lambda = 2537 \text{ \AA}$ , an Hanovia SC 2537 low pressure mercury lamp with a 2 mm Corning 7910 glass filter; and (c) for  $\lambda = 3261 \text{ \AA}$ , a cadmium Phillips spectral lamp with a 5 mm Corning 7910 glass filter.

## III. EXPERIMENTAL RESULTS

Experiments with DBr + HBr + He mixtures were conducted at 2138 and 2537  $\text{\AA}$ . Experiments with DI + HI + He mixtures were conducted at 2537 and 3261  $\text{\AA}$ . The experimental results are shown in Fig. 1. As can be seen, the dependence of  $[H_2]/[HD]$  on  $([HX]+[DX])/[He]$  is not linear. This is different from the results in Ref. 1 where a linear dependence was found for the  $[D_2]/[HD]$  ratio on the  $[DX]/[He]$  ratio. The nonlinearity in the present experiments is probably due to the high  $[DX]/[HX]$  ratios used, necessitated, as described in the introduction, by the smallness of the  $\epsilon_{DX}/\epsilon_{HX}$  extinction coefficient ratio. The mechanism given by Reactions (1), (2), and (5)–(13) plus the additional H\* and D\* reactions lead to a very complicated nonlinear kinetic expression for  $[H_2]/[HD]$  as a function of  $([HX]+[DX])/[He]$  involving an appreciable number of unknown hot atom rate coefficients. Therefore, rather than try to fit such an expression to our measurements, we did experiments down to relatively low  $([HX]+[DX])/[He]$  values and performed a smooth extrapolation to a vanishing value of this ratio. Since this extrapolation was purely empirical, we made a liberal allowance for the uncertainty of the resulting value of  $([H_2]/[HD])_0$ , as indicated by the dashed lines in Fig. 1. This turned out to be the major contribution to

TABLE I. Summary of results of photolysis of HX+DX+He mixtures. The  $([H_2]/[HD])_0$  are the extrapolated values of the curves in Fig. 1 to  $([HX]+[DX])/[He] = 0$ .

Halogen X	$\beta = [DX]/[HX]$	$\lambda (\text{\AA})$	$Y = \epsilon_{DX}/\epsilon_{HX}^a$	$([H_2]/[HD])_0$	$([HD]/[H_2])_0$
Br	0.239 <sub>6</sub>	2138	0.70 <sub>4</sub> ± 0.01 <sub>1</sub>	3.8 <sub>5</sub> ± 0.1 <sub>5</sub>	0.26 <sub>0</sub> ± 0.01 <sub>0</sub>
	± 0.001 <sub>9</sub>	2537	0.147 ± 0.007	6.30 ± 0.1 <sub>5</sub>	0.159 ± 0.004
I	0.234 <sub>4</sub>	2537	0.877 ± 0.009	2.87 ± 0.05	0.348 ± 0.006
	± 0.001 <sub>9</sub>	3261	0.141 ± 0.007	5.1 <sub>0</sub> ± 0.2 <sub>0</sub>	0.196 ± 0.008

<sup>a</sup>Values taken from Ref. 1 except for the value for HI + DI at 2537  $\text{\AA}$  which was a private communication from J. A. Betts, D. R. Davis, J. M. White, and A. Kuppermann.

the error in  $a$  (D + HX) with  $a$  (H + DX), as described in the following.

In Table I we give the values of  $([H_2]/[HD])_0$  and their inverse, the corresponding uncertainties, and the values of  $\beta$ ,  $\lambda$ , and  $Y$  for  $X = \text{Br}$  and  $\text{I}$ . The values of  $([HD]/[H_2])_0$  are used to evaluate the rate constant ratios  $k_1/k_{11}$ ,  $k_{11}/k_5$ ,  $k_6/k_5$ , and  $k_2/k_1$  by the method outlined below. It involves Eq. (15) for two wavelengths,

$$\left(\frac{[HD]}{[H_2]}\right)_{0,\lambda_1} = M + \beta Y_1 \frac{1 + M(1 + \beta k_{11}/k_5) - \beta^2 \gamma (k_{11}/k_5)^2}{1 + \beta k_{11}/k_5 + (1 + Y_1 \beta) k_6/k_5}, \quad (15')$$

$$\left(\frac{[HD]}{[H_2]}\right)_{0,\lambda_2} = M + \beta Y_2 \frac{1 + M(1 + \beta k_{11}/k_5) - \beta^2 \gamma (k_{11}/k_5)^2}{1 + \beta k_{11}/k_5 + (1 + Y_2 \beta) k_6/k_5}. \quad (15'')$$

In addition, Eqs. (16) and (17) and the relations

$$\frac{k_1}{k_{11}} = \frac{k_1}{k_{12}} \frac{k_{12}}{k_{11}} = \gamma \frac{k_{11}}{k_5} \frac{k_{12}}{k_{11}} \quad (18)$$

and

$$k_2/k_1 = \frac{k_6/k_5}{(k_{11}/k_5)(k_6/k_2)(k_1/k_{11})} \quad (19)$$

are used. As will be shown below,  $k_{12}/k_{11}$  and  $k_6/k_2$  can be evaluated from independent experimental kinetic data and from equilibrium statistical mechanics. It will also be shown that to within about 10% accuracy, the value of  $\gamma$  defined by Eq. (17) is unity,

$$\gamma = 1. \quad (20)$$

Under these conditions, the only unknowns in the five equations (15'), (15''), (16), (18), and (19) are  $M$ ,  $k_1/k_{11}$ ,  $k_{11}/k_5$ ,  $k_6/k_5$ , and  $k_2/k_1$ . These equations can therefore be solved by an iterative procedure to yield the unknowns.

The ratio  $k_{12}/k_{11}$ , needed to implement this procedure, is calculated from the ratio of rate constants for the reverse reactions and the ratio of equilibrium constants for Reactions (12) and (11) according to

$$\frac{k_{12}}{k_{11}} = \frac{k_{X+H_2}}{k_{X+D_2}} \frac{Q_{H_2}}{Q_{D_2}} \frac{Q_{DX}}{Q_{HX}}, \quad (21)$$

where the  $Q$ 's are partition functions which are calculated by the method outlined by Bigeleisen and Mayer,<sup>2</sup> using spectroscopic data from Herzberg.<sup>3</sup> At 300 °K we get  $Q_{H_2}/Q_{D_2} = 0.073$ ,  $Q_{DBr}/Q_{HBr} = 4.31$ , and  $Q_{DI}/Q_{HI} = 3.43$ . Corrections for anharmonicity and for nonclassical behavior of rotational partition functions of  $H_2$  and  $D_2$  are included. The ratio  $k_{Br+H_2}/k_{Br+D_2}$  is obtained by extrapolating the experimental data of Timmons and Weston<sup>4</sup> to 300 °K. Similarly, the ratio  $k_{I+H_2}/k_{I+D_2}$  is obtained from the data of Sullivan.<sup>5</sup> The resulting values calculated for  $k_{12}/k_{11}$  are included in Table II. The relatively large error limits reflect the uncertainty in the extrapolation of  $k_{X+H_2}/k_{X+D_2}$  from high temperatures (438–623 °K for  $X = \text{Br}$  and 633–800 °K for  $X = \text{I}$ ) to 300 °K.

The rate constant ratio  $k_6/k_2$  is the equilibrium constant for Reaction (6) and therefore equal to the ratio of partition functions  $Q_{DX}/Q_{HX}$ . Its values, calculated as indicated above, are also listed in Table II.

The quantity  $\gamma$  defined by Eq. (17) can be estimated from the transition state theory if information about the potential energy surface for the  $H_2X$  system is available, or can be obtained directly from experiment for cases for which sufficient kinetic isotope effects have been measured. According to transition state theory we may write

$$\gamma = Q_{HDX}^\ddagger Q_{DHX}^\ddagger / Q_{DDX}^\ddagger Q_{HHX}^\ddagger. \quad (22)$$

The  $Q^\ddagger$ 's are transition state partition functions, the partition functions for the reagents having cancelled out.

For  $X = \text{Br}$ , Timmons and Weston<sup>4</sup> have obtained transition state force constants and internuclear distances by fitting transition state theory to kinetic isotope effect data ( $\text{Br} + H_2$ ,  $D_2$ ,  $HD$ , and  $HT$ ). We used their  $A$  and  $C$  empirical sets of force constants (Fig. 4 and Table II of Ref. 5) and with the aid of equations similar to their Eqs. (12)–(15) we obtained the values  $k_{11}/k_5 = 0.44$  and  $k_1/k_{12} = 0.44$  (average over the two sets) in agreement with Eq. (20).

For  $X = \text{Cl}$ , enough data are available to calculate  $\gamma$  both from experiment and from transition state theory. Using available data for  $k_{-12}/(k_{-5} + k_{-1})$ ,<sup>6-8</sup>  $k_{-12}/k_{-11}$ ,<sup>8</sup> and  $k_{-5}/k_{-1}$ <sup>10</sup> and ratios of equilibrium constants from statistical mechanics, we obtained  $\gamma = 0.91 \pm 0.04$ , again in agreement with (20). In addition, using several LEPS potential energy surfaces for this system<sup>8,10</sup> as well as BEBO and empirical parameters the value of  $\gamma$  obtained

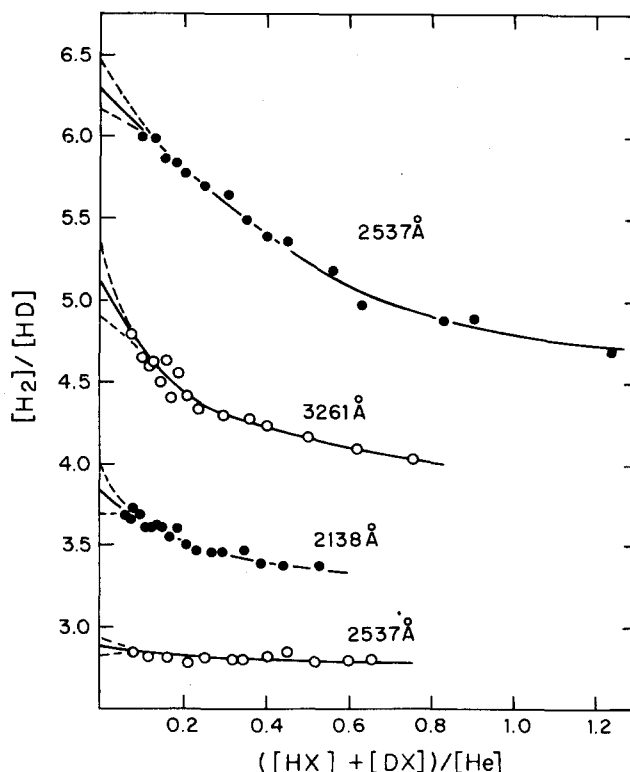


FIG. 1. Plots of  $[H_2]/[HD]$  as a function of  $([HX] + [DX])/[He]$  for the photolysis of  $HX + DX + He$  mixtures at the indicated wavelengths  $\circ$ ,  $X = \text{Br}$ ;  $\bullet$ ,  $X = \text{I}$ .

TABLE II. Summary of abstraction fractions and of ratios of rate constants in the photolysis of  $\text{HX} + \text{DX} + \text{He}$  mixtures ( $\text{X} = \text{Br}, \text{I}$ ).

X	Br	I
$k_{12}/k_{11}^a$	$3.4 \pm 0.4$	$1.9 \pm 0.6$
$k_6/k_2^b$	4.31	3.43
$M$	$0.132 \pm 0.007$	$0.16_6 \pm 0.01_0$
$k_1/k_{11}$	$1.8 \pm 0.3$	$1.3 \pm 0.4$
$k_{11}/k_5 (\approx k_1/k_{12})^c$	$0.53 \pm 0.02$	$0.68 \pm 0.04$
$k_6/k_5$	$0.31 \pm 0.1_8$	$0.14 \pm 0.1_0$
$k_2/k_1$	$0.08 \pm 0.04$	$0.05 \pm 0.04$
$a(\text{D} + \text{HX}) = k_5/(k_5 + k_6)$	$0.7_6 \pm 0.1_0$	$0.88 \pm 0.08$
$a(\text{H} + \text{DX}) = k_1/(k_1 + k_2)$	$0.93 \pm 0.04$	$0.96 \pm 0.04$
$a(\text{H} + \text{DX})$ Ref. 1	$0.99 \pm 0.03$	$0.97 \pm 0.05$

<sup>a</sup>Calculated from the ratio of rate constants for the reverse reactions and the ratio of equilibrium constants for Reactions (12) and (11).

<sup>b</sup>Calculated from equilibrium statistical mechanics.

<sup>c</sup>As justified in the text  $k_1/k_{12}$  is assumed to be equal to  $k_{11}/k_5$  to within about 10% accuracy.

from transition state theory was unity within 10%. In view of these results for  $\text{X} = \text{Br}$  and  $\text{X} = \text{Cl}$ , and of the fact that, as shown below, the abstraction fractions  $a(\text{D} + \text{HX})$  and  $a(\text{H} + \text{DX})$  are relatively insensitive to  $\tau$ , we have adopted the value  $\tau = 1.0 \pm 0.1$  for  $\text{X} = \text{I}$  as well.

The values of  $M$ ,  $k_1/k_{11}$ ,  $k_{11}/k_5$ ,  $k_6/k_5$ , and  $k_2/k_1$  obtained by the procedure described above are presented in Table II. Also included in it are the values of the abstraction fractions  $a(\text{D} + \text{HX})$  and  $a(\text{H} + \text{DX})$  calculated by Eqs. (4) and (3), respectively. The results obtained for  $a(\text{H} + \text{DX})$  agree within experimental errors with those of Ref. 1, which were obtained, as mentioned in Sec. I, using much smaller  $[\text{HX}]/[\text{DX}]$  ratios. This agreement can be considered as a self-consistency check of the present method.

#### IV. ERROR ANALYSIS

The main contribution to the relatively large standard relative errors in  $k_6/k_5$  comes from errors in  $([\text{H}_2]/[\text{HD}])_0$  (given in Table I), which result from the extrapolation procedure to vanishing  $([\text{HX}] + [\text{DX}])/[\text{He}]$  as discussed at the beginning of Sec. III. The other sources of error are significantly smaller. For example, for  $\text{X} = \text{Br}$ , changing  $k_{11}/k_5$  from 0.53 to 0.44 changes  $k_6/k_5$  from  $0.31 \pm 0.1_8$  to  $0.3_3 \pm 0.1_8$  and  $a(\text{D} + \text{HBr})$  from  $0.7_6 \pm 0.1_0$  to  $0.7_5 \pm 0.1_0$ . For  $\text{X} = \text{I}$ , an analogous change of  $k_{11}/k_5$  from 0.68 to 0.60 changes  $k_6/k_5$  from  $0.14 \pm 0.1_0$  to  $0.1_5 \pm 0.1_0$  and  $a(\text{D} + \text{HI})$  from  $0.88 \pm 0.08$  to  $0.87 \pm 0.08$ . The contributions of the uncertainties in  $\tau$  and in the other experimentally determined quantities to the absolute errors in  $a(\text{D} + \text{HX})$  are each about an order of magnitude smaller than that of  $([\text{H}_2]/[\text{HD}])_0$ .

Similarly, the main contribution to the error in  $k_2/k_1$  and  $a(\text{H} + \text{DX})$  stems from the uncertainty in  $([\text{H}_2]/[\text{HD}])_0$ . In addition, however, an error of comparable magnitude results from  $k_1/k_{11}$  via  $k_{12}/k_{11}$ .

The relative errors in  $k_6/k_5$  (55% and 70%) and  $k_2/k_1$  (50% and 80%) are quite large. However, a favorable error propagation condition produces values of the abstraction fractions  $a(\text{D} + \text{HX})$  and  $a(\text{H} + \text{DX})$  which have estimated accuracies of 13% and 9% for the former and 4% and 3% for the latter, for  $\text{X} = \text{Br}$  and  $\text{I}$ , respectively. These errors are sufficiently small to make the values of  $a$  thus determined useful. Experiments at values of  $([\text{HX}] + [\text{DX}])/[\text{He}]$  down to 0.02 would significantly decrease the errors in the values of  $a$  here reported.

#### V. DISCUSSION

The main motivation for the experimental determination of  $a(\text{D} + \text{HX})$  reported here was the fact that it was needed in connection with a study of the energy dependence of the integral reaction yield for the  $\text{H}^* + \text{D}_2 \rightarrow \text{HD} + \text{D}$  reaction.<sup>11</sup> In addition, however, it merits consideration on its own right. The values of  $a(\text{H} + \text{DX})$  summarized in Table II are characterized by the fact that they are quite close to unity both for  $\text{X} = \text{Br}$  and  $\text{X} = \text{I}$ . On the other hand, the value of  $a(\text{D} + \text{HX})$  is  $0.7_6 \pm 0.1_0$  for  $\text{X} = \text{Br}$  and  $0.88 \pm 0.08$  for  $\text{X} = \text{I}$ . It is interesting to speculate on what causes this isotope effect and its dependence on  $\text{X}$ . The reason that  $a(\text{H} + \text{DX})$  is close to unity is that the corresponding exchange reaction is slightly endothermic (by 1.09 and 0.96 kcal/mole for  $\text{X} = \text{I}$  and  $\text{Br}$ , respectively) whereas the abstraction one is very exothermic (by 16.37 and 32.59 kcal/mole for  $\text{X} = \text{Br}$  and  $\text{I}$ , respectively), in addition to having a small activation energy (see Table VI of Ref. 12). As a result, from the phase space theory perspective,<sup>12</sup> the exchange reaction is much less likely to occur than the abstraction one. As one now considers the isotopically reversed  $\text{D} + \text{HX}$  processes, the exchange reaction is slightly exothermic (by 1.09 and 0.96 kcal/mole for  $\text{X} = \text{I}$  and  $\text{Br}$ , respectively) whereas the abstraction one is still highly exothermic (17.46 and 33.55 kcal/mole for  $\text{X} = \text{Br}$  and  $\text{I}$  respectively). These changes should have a more pronounced effect, at 300 °K, in enhancing the rate constants of the exchange reaction than the abstraction one, and this effect should be relatively larger on the  $\text{X} = \text{Br}$  system than on the  $\text{X} = \text{I}$  system (because of the relative exothermicities of the corresponding abstraction reactions). As a result,  $a(\text{D} + \text{HX})$  should be smaller than  $a(\text{H} + \text{DX})$  and the decrease should be greater for  $\text{X} = \text{Br}$  than for  $\text{X} = \text{I}$ , in qualitative agreement with the present experimental results. These measurements can serve as a basis for testing theories of chemical dynamics which are able to predict the outcome of the competition between different exit channels, such as the statistical phase space theory, quasiclassical trajectory calculations, semiclassical theory, and quantum-dynamical calculations.

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