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# Isotope effects and excitation functions for the reactions of $S(^{1}D) + H_{2}$ , $D_{2}$ and HD

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#### Abstract

Excitation functions for the title reactions were determined from 0.6 to 6 kcal/mol. Contrary to the analogous reaction of  $O(^{1}D)$ , it appears that the reaction of  $S(^{1}D)$  proceeds solely through insertion over this energy range. Compared to other reactions, an intriguing H/D isotope effect was revealed. The propensity of the intramolecular H/D branching found under thermal conditions for A + HD reactions appears to be reverse for a supersonically cooled HD reagent. This finding implies that the reagent rotation could have profound influences on radical reactivity not only for an activated abstraction reaction, but for a barrierless inserted one. © 1998 Elsevier Science B.V. All rights reserved.

# 1. Introduction

The elementary chemical reaction can be classified according to its reaction mechanism as a direct abstraction, an (end-on) addition–elimination, or an (edge-on) insertion–decomposition process, with the latter two involving the formation of reaction complexes. Knowledge accumulated over the past decades in reaction dynamics allow us now to make some generalizations or to 'understand' many of dynamical attributes based on this simple classification and its relationship to the dominant features of the potential energy surface (PES) involved.

One aspect, which has recently received considerable attention both experimentally and theoretically, is the isotope branching ratio, in particular for the reaction with HD. In a seminal paper [1], Bersohn and coworkers summarized the intramolecular H/D branching measured for the room-temperature average of the ratio of the rate constants for the two exit channels of the A + HD reaction. They found that for a direct abstraction reaction with an entrance channel barrier, such as F + HD, this ratio is usually less than one. By contrast, a ratio of larger than one was generally found for a number of reactions which are believed to proceed through an insertion mechanism (some of them are known to have little potential energy barrier). Qualitative arguments, based on either the screening of the D atom by the H atom in a rotating HD molecule or the escape probability from a HAD complex, were also presented to rationalize the observations.

Subsequent theoretical investigations [2–8], based on quasi-classical trajectory (QCT) results for a few direct abstraction reactions, indicated that the interpretation is actually far more complicated. The H/Dratio depends not only sensitively on the shape of the PES en route to the barrier (i.e. oblate vs. prolate),

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but also on the reagent rotation. The reader is referred to Ref. [2] for an excellent review. Although conflicting conclusions still remained [8-11] regarding the exact interpretations of the role of reagent rotation on reactivity, it is generally accepted that the rotational effect is intimately related to stereodynamics.

As to insertion reactions, either with or without a barrier, much less has been investigated theoretically. In a very illuminating QCT study of the reaction dynamics for  $O(^{1}D) + H_{2}$ ,  $D_{2}$  and HD [12], Schatz and coworkers found the intramolecular isotope effect is strongly dependent on PES. The H/Dratio varies from  $\sim 1.0$  for the MC (Murrell and Carter) surface to  $\sim 1.8$  for the SL (Schinke and Lester) surface. A detailed analysis of the reaction mechanism was also performed to elucidate the mechanistic origin of the difference. It is now probably well-accepted that the reaction of  $O(^{1}D) + H_{2}$  is complicated by the additional microscopic abstraction pathway which proceeds initially on excited surfaces [13,14]. The presence of a collinear barrier of ~2 kcal/mol on the excited surface [13,14] makes the direct comparison of the H/D ratio more complicated between theory (if only the ground state surface of H<sub>2</sub>O is considered) and experimental results (if the initial collision energy is too high or too broad). Nevertheless, the aforementioned theoretical investigation is, by itself, quite insightful in that it clearly showed that just like a direct abstraction reaction, the long range orientation effects in the entrance channel can have profound influences on the observed H/D ratio for an inserted one, at least for a reaction in which a short-lived complex is involved such as  $O(^{1}D) + HD$  [12]. If this conclusion is accepted, then the effects of rotational stereoselectivity might also be anticipated for an insertion reaction. On the other hand, if the complex lives sufficiently long, one might expect the dynamics being governed by the complex decomposition and all initial memories being lost. No reagent rotation effect is then anticipated.

Reported here is our continuing efforts in understanding insertion reactions. The system studied is the reactions of  $S(^{1}D)$  atom with  $H_{2}$  and its isotopomers,  $S(^{1}D) + H_{2} \rightarrow SH(X^{2}\Pi) + H$ . Analogous to the reaction of  $O(^{1}D)$ , the interactions of the divalent  $S(^{1}D)$  radical with  $H_{2}$  lead to the reaction

complex of H<sub>2</sub>S on the ground state PES through the insertion mechanism. The product is formed via subsequent complex decomposition. The well-depths of reaction complexes, H<sub>2</sub>O and H<sub>2</sub>S, for both reactions are quite comparable, 118 and 90 kcal/mol, respectively (reference to the product channel). The exoergicity for the present system is, however, substantially smaller than that for  $O(^{1}D) + H_{2}$ , 6–7 vs.  $\sim 43$  kcal/mol. Because of the deep potential well and the small exoergicity, conventional wisdom will then predict a long-lived complex being involved in the title reaction and the statistical behavior might be borne out [15]. Indeed, this is the conclusion drawn from the measured isotope branching ratio and translational energy release in a recent investigation of this reaction [16]. That study was conducted by the hot  $S(^{1}D)$ -atom technique in a room temperature cell, thus the initial collision energy distribution is relatively broad. Similar to the case of  $O(^{1}D)$ , five PESs are involved in the interactions of  $S(^{1}D)$  with H<sub>2</sub>. The degree of the participation of excited surfaces, which roughly speaking correspond to the abstraction channel, in reactivity is unknown. The questions we would like to address here are, over what energy range does one need to consider the abstraction pathway? What are the isotope branchings for the insertion and abstraction pathways, respectively? How do they compare with other reaction systems?

### 2. Experiment

The experiment was carried out in a crossed-beam apparatus with the procedure similar to that reported previously for the analogous reaction of O(<sup>1</sup>D) [14]. In brief, a skimmed S(<sup>1</sup>D) beam was generated by laser photolysis of CS<sub>2</sub> ( $\leq 0.5\%$  CS<sub>2</sub> seeded in He at stagnation pressure of 15 atm.) at 193 nm (ArF laser) near the throat of a piezoelectric pulsed valve. The subsequent supersonic expansion confined and translationally cooled the S(<sup>1</sup>D) beam which then collided with the target molecules (H<sub>2</sub>, D<sub>2</sub> and HD) from the second pulsed beam. By alternating the target gas pulses and taking the difference signal, the reaction product of the H or D atom was interrogated by a (1 + 1) resonance-enhanced multiphoton ionization/time-of-flight mass spectrometric detection

scheme. The 121.6 nm vacuum ultraviolet (VUV) photon for the H or D atom Lyman-α transition was generated by the frequency tripling technique from the input UV light ( $\sim 365$  nm) in a Kr gas cell. One unique feature of this apparatus is the ease in controlling the initial collision energy by merely changing the intersection angle of the two molecular beams without changing any other source parameters. The translational energy resolution in this work was governed by the velocity spreads and the angular divergences of the two skimmed molecular beams, and was determined to be about 10% ( $\Delta E_{\perp}/E_{\perp}$ ). By virtue of the ortho/para nature of hydrogen (deuterium) molecule, the supersonic expansion does not relax the rotational degree of freedom fully. The average rotational energies of the target molecules were estimated to be 0.3 kcal/mol (Tr  $\sim$  150 K). 0.16 kcal/mol ( $\sim$  100 K) and 0.05 kcal/mol ( $\sim$  50 K) for  $H_2$ ,  $D_2$  and HD, respectively, as detailed previously [14].

The experiment was performed in the following way. At a given beam-intersection angle (i.e. initial collision energy), the probe laser wavelength was scanned. By integrating the difference signals over the entire Doppler profile, which is proportional to the total reaction rate at a given collision energy, the reaction excitation function, i.e. the translational energy dependencies of the total reaction cross-sections, is readily obtained by repeating the measurements at different intersection angles. Several backto-back wavelengths scans at fixed intersection angles were performed for normalizing the reaction cross-sections for different isotopomers. For that purpose, care was taken to ensure that the experimental conditions were identical, in addition a 1:1 mixture of H<sub>2</sub> and D<sub>2</sub> was used to check the normalization factors and to cover a wider energy range. The uncertainties in relative cross-section measurements are all within  $\pm 5\%$ . The estimated overall errors are probably less than  $\pm 10\%$ .

#### 3. Results and discussion

Fig. 1a summarizes the excitation functions for the reactions of  $S(^{1}D) + H_{2}$ ,  $D_{2}$  and HD. The collision energy here,  $E_{c}$ , refers to the translational energy of the reagents. The small rotational energy of Fig. 1. (a) Excitation functions for the reactions of  $S({}^{1}D) + H_{2} \rightarrow SH + H$  (labeled as  $H_{2}$ , ( $\bigcirc$ ),  $S({}^{1}D) + D_{2} \rightarrow SD + D$  (as  $D_{2}$ , O),  $S({}^{1}D) + HD \rightarrow SD + H$  (as HD,  $\Box$ ) and  $S({}^{1}D) + HD \rightarrow SH + D$  (as HD,  $\blacksquare$ ). For clarity the results for HD are scaled up by two as indicated. The solid lines are the best-fits based on the empirical form (1) from Table 1. (b) The ratio of H/D yield for the  $S({}^{1}D) + H_{2}/S({}^{1}D) + D_{2}$  reactions (dashed line obtained from the fits in (a)) and for the SD + H/SH + D product channels in the  $S({}^{1}D) + HD$  reaction (the points are the experimental ratios and the solid line is from the fits in (a)).

the target molecule is not included. Contrary to the analogous reactions for  $O(^{1}D)$  [12], which all show an unusual behavior (i.e. rapid fall-off in reactivity followed by a gradual rise as the collision energy increases), in the present case the reaction cross-section decreases monotonically with the increase in collision energy. This behavior is characteristic of a reaction governed by long range attractive force with little potential barrier [15]. In consistency with the interpretation proposed for the  $O(^{1}D)$  reaction that the gradual rise in excitation function signifies the participation of an additional abstraction pathway at higher energies, the lack of such a signature in the present case implies little contribution from abstraction. Presumably, it is because the collinear barrier



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Table 1 Fitting parameters for the excitation function  $S(^{1}D)$  with  $H_{2}$  and its isotopomers

Parameter	H <sub>2</sub>	D <sub>2</sub>	HD	HD			
Function (1): $A_1 + A_2 \exp(-E_c / A_3)$							
$A_1$	6.70	7.37	6.56	8.58			
$A_2$	16.5	30.5	38.1	46.0			
$A_3$	0.66	0.89	0.56	0.60			
Function (2): $a_1 E_c^{-1} + a_2 E_c^n$							
$a_1$	7.41	15.4	11.9	16.0			
$a_2$	2.57	1.96	0.88	1.22			
n	0.5	0.5	1	1			

Note:  $E_c$  in kcal/mol.

height on the excited surface increases significantly as one shifts from  $O(^{1}D)$  to  $S(^{1}D)$ .

The notion that only the insertion pathway needs to be considered in the present case is also supported by the isotope branching ratio, as shown in Fig. 1b. The H/D ratios remain nearly constant over the



Fig. 2. The beam-derived rate constants based on the fits shown in Fig. 1. The results are normalized to the kinetics data, the circle  $(\bigcirc)$ , for S(<sup>1</sup>D)+H<sub>2</sub> at 300 K [17]. The symbols are the same as Fig. 1.



Fig. 3. Same as Fig. 1, except an alternate form (Function (2) in Table 1) was used in fitting the experimental data.

entire energy range of this work, which is exactly in accord with what was found previously for the reactions of  $O(^{1}D)$  at lower energies below the onset of the abstraction pathway.

To facilitate the comparison with future thermal rate constant measurements, attempt was made to fit measured excitation functions, as exemplified in Fig. 1 as the solid lines. The empirical form used is  $\sigma(E_{\rm c}) = A_1 + A_2 \exp(-E_{\rm c}/A_3)$  and the fitting parameters are summarized in Table 1. The Boltzmann-averaged thermal rate constants along with the kinetic isotope ratios are depicted in Fig. 2. As can be seen, the predicted rate constants show little temperature dependencies. Considering the large rate constant measured at 300 K,  $2.1 \times 10^{-10}$  $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup> [17] which is essentially gas kinetic, such a result is not surprising. Nevertheless, it should be commented that the valid temperature range of predicted rate constants depends somewhat on the empirical form used in fitting excitation functions, in addition to the intrinsic assumption that the



Fig. 4. The predicted thermal rate constants based on the fits shown in Fig. 3.

thermal Boltzmann average over the translational degree of freedom alone is sufficient. Shown in Fig. 3 is an alternative fit, where the empirical form of  $\sigma(E_c) = a_1 E_c^{-1} + a_2 E_c^n$  is adapted, and the fitting parameters are also listed in Table 1. Clearly, the fits to the data are as good as those depicted in Fig. 1. The only significant difference between the two fits lies in the low energy extrapolation. As a result, the predicted low temperature rate constants rise rapidly, Fig. 4. Due to the extrapolation uncertainty, we then conclude that the predicted rate constant will not be reliable for temperatures < 250 K. The same conclusion has been drawn for the previously reported results for the O(<sup>1</sup>D) reaction [14].

Perhaps the most surprising finding of this work is the isotope effect. First, the magnitudes of total reaction cross-sections follow an unusual trend,  $\sigma_{\rm HD} > \sigma_{\rm D2} > \sigma_{\rm H2}$ , over the entire energy range. Consequently the beam-derived rate constants become  $k_{\rm HD} > k_{\rm H2} \approx k_{\rm D2}$ , which is to be contrasted to the prediction of  $k_{\rm H2} > k_{\rm HD} > k_{\rm D2}$  from a simple transition state theory. Second, the intramolecular H/D iso-

tope ratio is about 0.7, which is noticeably smaller than the previously reported values of 0.9-1.0 under bulk conditions [16]. The latter is more in line with the statistical argument. That difference becomes more significant when one compares it with a few other currently available reaction systems under similar circumstances, as indicated in Table 2. As alluded to earlier, the thermal results led to the previous classification [1] that the H/D ratio is in general less than one for a direct abstraction reaction, whereas it is slightly larger than one for an inserted one. Under the crossed-beam conditions, the generalization appears to be reverse (!). Although the crossedbeam H/D ratios for insertion reactions.  $O(^{1}D)/S(^{1}D) + HD$ , still cluster around one, they tend to be on the lower side. The ratios for abstraction, on the other hand, are significantly larger than one, opposite to the thermal results.

The apparent discrepancy between two sets of data could be attributed to the rotationally cold HD reagent in crossed-beam experiments. The effects of the HD rotation on the H/D isotope branching ratio for an abstraction reaction with an entrance barrier have been amply discussed theoretically in the literatures [2–8], most notably for the reaction F + HD. While the room temperature kinetics measurements yielded H/D = 0.8 [20], the QCT calculation on the most accurate ab initio SW–PES found a strong dependency of this ratio on the HD rotational state,

Table 2

Intramolecular isotope branching ratio (H/D) for the reaction of A + HD

A	H/D		Refs.
	(crossed-beam)	('thermal')	
$S(^{1}D)$	$0.72 \pm 0.07$	0.9-1.0	[16]
$O(^{1}D)$	$1.17 \pm 0.1$ (insertion) <sup>a</sup>	$1.33 \pm 0.08$	[18]
		$1.13\pm0.07$	[1]
	~ 2.8 (abstraction) <sup>a</sup>		
Cl	~ 3 <sup>b</sup>	$\sim 0.6$	[19]
F	1.2-3 <sup>c</sup>	$\sim 0.8$	[20]

<sup>a</sup> From Ref. [14]. There is a small error in the previously reported result. The cross-sections for  $O(^{1}D) + HD \rightarrow OD + H$  should be scaled up by 1.15.

<sup>b</sup>From this laboratory [21], the H/D ratio actually depends on the collision energy. The quoted value here represents the mean value. <sup>c</sup> No crossed-beam data available. The quoted values are the QCT result for HD (v = 0, j = 0) from Ref. [7], its variation arises from the collision energy dependency. and for HD (v = 0, i = 0) it also varied from ~ 3 to 1.2 with the collision energy [7]. The mass asymmetry effects discussed in details by Johnston et al. [3] clearly play the dominant role in favor of the FD formation for i = 0 at low energies. The decrease of the H/D ratio with collision energy was accounted for by the long range reorientation effects on the SW-PES [7]. Theoretical investigations for several other abstraction reactions, such as H + HD [6] and Cl + HD [4,5], on various types of PESs all have reached similar conclusions: at low *j*, the D-end is preferentially abstracted. The crossed-beam results reported in Table 2 represent the first few experimental confirmations of this theoretical prediction. Interestingly, when HD is rotationally excited, the opposite propensity is often observed as in the thermal measurements. Thus, the contrast between the supersonic crossed-beam and thermal data on the H/D ratio suggests a sensitive means to gain deeper insights into the interplay of the relevant topological feature of PES and rotational stereoselectivity.

By comparisons, the agreement between the two sets of measurements for insertion reactions seems somewhat better. However, the ratio of ca. 0.7 for the title reaction from this work clearly does not fall into the 'larger than one' category based on the previous generalization [1] and is also not in line with the statistical expectation. If a short-lived complex is invoked in this reaction, it is conceivable that the discrepancy could arise from the rotational effects as well, just like the direct abstraction reaction though the effects might be opposite for a barrierless insertion pathway. However, the notion of a shortlived complex is in conflict with conventional wisdom in view of the energetics along the reaction path for  $S(^{1}D) + HD$ . On the other hand, if the reaction indeed proceeds through a long-lived complex, all initial memory will be lost. The rotational effects should be diminished and the crossed-beam ratio should have agreed with the thermal one. Clearly more work, both experimentally and theoretically, is needed in clarifying this paradox. Further work to characterize the differential cross-section for this reaction is currently in progress in this laboratory.

In summary, from the shape of the measured excitation functions it is conjectured that the title reactions proceed predominantly via insertion pathway for collision energy up to ca. 6 kcal/mol.

Compared to a few other currently available reaction systems under either the crossed-beam or the 'thermal' condition, intriguing intramolecular isotope effects are revealed. The discernible 'less than one' H/D ratio for the title reaction calls for further investigation.

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