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The dynamics of the OH + HD gas-phase reaction: absolute reaction cross section and H/D atom product branching ratio

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Abstract

The dynamics of the OH + HD reaction were studied in the gas-phase using the laser photolysis/vacuum-UV laser-induced fluorescence "pump-and-probe" technique. Translationally energetic OH(²Π) radicals with an average reagent translational energy of $E_{c.m.} = 0.24$ eV in the (OH-HD)-center-of-mass system were generated by the laser photolysis of H₂O₂ at 248 nm. Doppler profiles of nascent D and H atoms produced in reactive collisions of OH with room-temperature HD molecules were detected under single-collision conditions by VUV-LIF at the Lyman- α transition. For the OH + HD reaction an absolute reaction cross section of $\sigma_R(0.24 \text{ eV}) = (0.14 \pm 0.05) \text{ Å}^2$ was determined by means of a calibration method using OH + D₂ as a reference reaction. The branching ratio for the OH + HD \rightarrow H + HOD (D + H₂O) product channels was measured to be $\Gamma_{H/D} = (1.2 \pm 0.2)$. © 1997 Elsevier Science B.V.

1. Introduction

The gas-phase reaction of the $OH(^{2}\Pi)$ free radical with molecular hydrogen

$$OH + H_2 \rightarrow H + H_2O$$
, $\Delta H_0 = -14.8 \text{ kcal/mol}$
(1)

plays an important role in combustion [1] and atmospheric chemistry [2]. In addition, the OH + H_2 reaction and its reverse H + H_2O have become benchmark systems for the development of rigorous quantum mechanical diatom-diatom and atom-triatom scattering methods [3,4].

For the reaction of H atoms with $H_2O/D_2O/HOD$, the influence of selective reagent

translational and vibrational excitation on the reactivity has been studied in great detail [5-13]. Investigations of the partially isotopically substituted $H + D_2O$ reaction in which absolute reactive cross sections for the HD + OD and D_2 + OH product channels were measured [7,14] showed that the $H + H_2O \rightarrow H_2 +$ OH reaction proceeds almost exclusively by a direct abstraction mechanism via a planar H-H-O-H transition, state rather than via the formation of a H_3O intermediate. Only recently could experimental studies of the gas-phase reaction dynamics of the hydrogen atom exchange pathway $H + D_2O \rightarrow HOD + D$ be carried out which revealed that the absolute reactive cross section for hydrogen exchange is considerably higher than that for the hydrogen abstraction channel [15]. Using a combination of single-collision reaction cross section, H atom moderation and non-

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equilibrium D atom formation rate measurements, the reaction threshold and the excitation function for the $H + D_2O \rightarrow D + HOD$ exchange reaction were determined [16].

Due to its key role in hydrogen combustion, numerous measurements of the thermal rate of the $OH + H_2$ reaction were carried out [17] covering the temperature range from 250 [18] to 3000 K [19]. Dynamics studies, where the influence of reagent translational excitation on the absolute reactive cross section of reaction (1) was investigated, are reported in Ref. [14]. In the same study, H/D product branching ratio measurements for the $OH + D_2$ reaction were reported which showed that D + HOD is the dominant reaction pathway. In crossed-molecularbeam studies of the $OH + D_2 \rightarrow D + HOD$ reaction a strongly backward-scattered (with respect to the OH direction) HOD angular distribution was observed [20], reflecting direct rebound dynamics. The results of Refs. [14,20] clearly indicate that the OH + H₂ reaction proceeds via a simple hydrogen abstraction mechanism through a tightly constrained transition state [21], in which the formation of the new H–OH bond occurs simultaneously with the cleavage of the old H–H bond [22]. The dynamics of the OH + HD, reaction which leads to distinguishable products, H + HOD and D + H_2O ,

$$OH + HD \rightarrow H + HOD,$$
 (2a)

$$OH + HD \rightarrow D + H_2O,$$
 (2b)

have so far only been studied theoretically using an accurate time-dependent quantum wavepacket (TD-QWP) method [23,24] on the Schatz-Elgersma potential energy surface (SE-PES) [25,26]. Due to the exact nature of the dynamical treatment a comparison of the quantum results with those obtained in experiments can yield detailed information on she accuracy of this PES.

The aim of the work to be presented in this Letter is to provide as yet undetermined experimental dynamical quantities such as an absolute reaction cross section and an isotope product branching ratio for the OH + HD reaction in order to allow comparison with the above mentioned accurate quantum scattering calculations.



Fig. 1. Schematic diagram of the experimental apparatus (LM: lens monochromator, PM: photomultiplier).

2. Experimental

Reaction dynamics studies were carried out in a flowing mixture of H_2O_2 and room temperature HD (Cambridge Isotope Laboratories, 98.6%) with the ratio of $[H_2O_2]$:[HD] typically being 1:2 at a total pressure of 100 mTorr using a flow reactor apparatus depicted schematically in Fig. 1. Similar experimental apparatus was used previously to measure absolute reaction cross sections and isotope branching ratios for the OH + H_2/D_2 [14] and O(¹D) + $H_2/D_2/HD$ reactions [27]. H_2Q_2 (PEROXID Chemie, 85%) was pumped through the reaction cell for at least 3 days to remove H_2O until it reached a final concentration of > 99.8% (determined by titration).

A KrF excimer laser $(\lambda_{pump''} = 248 \text{ nm})$ was used to dissociate H_2O_2 , generating translationally energetic OH radicals in the ² Π electronic ground state with an average translational energy of $E_{\text{c.m.}} =$ 0.24 eV in the (OH–HD) center-of-mass system. An aperture was used to skim off a homogeneous part of the rectangular excimer laser profile in order to provide a photolysis beam of about 2–5 mJ/pulse. The OH product rotational fine-structure state distribution measured in the 248 nm photolysis of H_2O_2 showed no preference population for either one of the two Λ -doublet components, ${}^2\Pi(\Lambda')/{}^2\Pi(\Lambda'') \approx 1$ [28].

VUV-probe laser radiation, tunable around the H (121.567 nm) and D (121.534 nm) atom Lyman- α

transitions, was generated using Wallenstein's method for resonant third-order sum-difference frequency conversion $(\omega_{VUV} = 2 \omega_R - \omega_T)$ of pulsed dye laser radiation (pulse duration ~ 15 ns) in a phase-matched Kr-Ar mixture [29], the frequency $\omega_{\rm R}$ ($\lambda_{\rm R} = 212.55$ nm) being resonant with the Kr 4p-5p (1/2, 0) two-photon transitions. ω_T could be tuned from 844 to 848 nm to cover the H and D atom Lyman- α transitions. The fundamental laser radiation was obtained from two tunable dye lasers, simultaneously pumped by a XeCl excimer laser, one of which, $\omega_{\rm R}$, was frequency doubled with a BBO II crystal. Lyman- α light was carefully separated from the fundamental lasers by a lens monochromator (LM in Fig. 1). The probe beam was aligned to overlap the photolysis beam at right angles in the viewing region of a LIF detector. The delay time between the photolysis and probe pulse was controlled by a pulse generator and could be monitored on a fast oscilloscope. Delay times between "pump" and "probe" laser pulses of (150 ± 5) ns were typically employed allowing the collision-free detection of the H and D atoms produced in the reaction. The H and D LIF signal was measured through a bandpass filter by a solar blind photomultiplier (PM1 in Fig. 1) positioned at right-angles to both the photolysis and probe lasers. The VUV-probe beam intensity was monitored after passing through the reaction cell with an additional solar blind photomultiplier (PM2 in Fig. 1). In order to obtain a satisfactory S/N ratio, each point of the H and D



in the $OH + D \rightarrow D + HOD$ reaction (b) D stoms prov

Fig. 2. Doppler profiles of (a) D atoms produced in the OH + $D_2 \rightarrow D$ + HOD reaction, (b) D atoms produced in the OH + HD \rightarrow D + H₂O reaction and (c) H atoms produced in the OH + HD \rightarrow H + HOD reaction. The LIF spectra are plotted against the wavenumber mismatch in units of cm⁻¹. Line centers correspond to the Lyman- α transition for the H atom (82259 cm⁻¹) and D atom (82281.5 cm⁻¹), respectively.

atom Doppler profiles (Fig. 2) was averaged over 30 laser shots. The measurements were carried out at a repetition rate of 6 Hz. The LIF signals, VUV-probe beam intensities and the photolysis intensity were recorded with a boxcar system and transferred to a microcomputer where the LIF Signal was normalized to both the photolysis and probe laser intensities.

It was found that the Lyman- α probe beam itself produced an appreciable H atom LIP signal via the photolysis of H₂O₂ alone [28]. In order to subtract these "background" H atoms from the H atoms produced in the 248 nm photolysis of the H₂O₂/HD mixture, an electronically controlled mechanical shutter was inserted into the photolysis beam path (see Fig. 1). At each point of the H atom line scan, the signal was first averaged with the shutter opened and again averaged with the shutter closed. A pointby-point subtraction procedure was adopted, to obtain directly and on-line a signal free from background "Lyman- α " H atoms.

3. Results and discussion

The total absolute reaction cross section for the OH + HD \rightarrow H + HOD (D + H₂O) reaction was obtained by means of a calibration method using the OH + D₂ \rightarrow D + HOD reaction, for which an absolute reaction cross section of $\sigma_{R}^{*} = (0.22 \pm 0.05) \text{ Å}^{2}$ has been measured in Ref. [14], as reference. By comparing the total H and D atom signal, $S_{H} + S_{D}$ (defined as the sum of the areas below the H and D atom Doppler profiles in Fig. 2b and c) produced in the reaction OH + HD, with the D atom signal S_{D}^{*} (defined as the area below the Doppler profile in Fig. 2a) produced in the OH + D₂ \rightarrow D + HOD reaction the total absolute reaction cross section σ_{R} for the OH + HD reaction can be obtained using the following formula:

$$\sigma_{\rm R} = \frac{S_{\rm H} + S_{\rm D}}{S_{\rm D}^*} \times \frac{v_{\rm rel}^*}{v_{\rm rel}} \times \sigma_{\rm R}^* \,. \tag{3}$$

Here v_{rel}^* and v_{rel} are the relative velocities corresponding to the average translational energies of $E_{c.m.} = 0.30 \text{ eV}$ and $E_{c.m.} = 0.24 \text{ eV}$ of the OH + D₂ and OH + HD reactant pairs. The average translational energies were calculated using the OH energy

partitioning data obtained in the 248 nm photodissociation studies of H_2O_2 as described in Ref. [31]. In Ref. [31] it was reported that the OH radicals are produced exclusively in the vibrational ground state with about 82% of the available energy going into OH translational motion. Due to the enhanced sensitivity of the present apparatus, in several runs small amounts of H atoms originating from the 248 nm photolysis of H_2O_2 , rather than from the OH + HD reaction could be observed [28]. In this case S_H has to be taken as the difference between the H atom signals observed upon irradiation of the H_2O_2/HD mixture and of H_2O_2 alone.

To determine the absolute reactive cross section for the OH + HD reaction, integrated areas under the H and D fluorescence curves were determined in a number of experimental runs under identical experimental conditions for the $OH + HD \rightarrow H + HOD$ (D + H₂O) and the OH + D₂ \rightarrow D + HOD reactions and evaluated using formula (3). Five independent calibration measurements which consisted of 15 individual H and D atom Doppler profiles yielded an average value for the OH + HD reaction cross section of $\sigma_{\rm R}(0.24 \text{ eV}) = (0.14 \pm 0.05) \text{ Å}^2$. The total experimental error was calculated from the errors of the entries of formula (3) on the basis of simple error propagation. The overall uncertainty of the calibration experiment — the measurement of $(S_{\rm H} +$ $(S_{\rm D})/S_{\rm D}^*$ — was determined to be 22% (one standard deviation). The uncertainty of $\sigma_{\rm R}^*$ was taken from Ref. [14].

The evaluation of the experimental data set yielded a branching ratio for the H + HOD and D + H₂O product channels of the OH + HD reaction of $\Gamma_{\rm H/D}$ = $S_{\rm H}/S_{\rm D} = (1.2 \pm 0.2)$. A comparison of the measured total reaction cross section and the product branching ratio $\Gamma_{\rm H/D}$ with the results of an accurate quantum scattering calculation on the SE-PES is shown in Fig. 3a and Fig. 3b, respectively. The theoretical cross Sections (dashed line in Fig. 3a) were obtained by multiplying the values given in Ref. [24] by a factor of 1/2 to account for the fact that only half of the reagent HD(${}^{1}\Sigma_{g}^{+}$) + OH(${}^{2}\Pi$) collisions access the reactive ${}^{2}A$ surface which correlates with the H(${}^{2}A'$) + HOD(${}^{1}A'$) and D(${}^{2}A'$) + H₂O(${}^{1}A'$) products [25].

When comparing with theory, one has to consider that because the experiments were carried out in the



Fig. 3. Comparison of (a) the experimental total absolute reaction cross section for the OH($j \approx 7$)+HD(T = 300 K) reaction and (b) the H versus D atom product branching ratio with the results of accurate quantum scattering calculations for the OH(j = 0)+ HD(j = 0) reaction [24] carried out on the SE-PES [25]. Filled squares represent values obtained by averaging the theoretical results (solid lines) over the underlying experimental reagents' translational energy distribution. Details about the influence of the thermal HD rotational excitation on the reaction cross section and the branching ratio are given in the text.

gas-phase at room temperature, the thermal motions of the OH precursor molecule (H_2O_2) and the HD target molecules leads to a broadening of the translational energy distribution in the OH–HD collision frame [30]. The underlying experimental reagents' translational energy distribution and its spread (± 0.1 eV) can be calculated using the OH energy partitioning data [31] and the formulae given in Ref. [32]. As a result, a range of collision energies contributes to the experimental quantities.

The measured absolute reactive cross section therefore contains "global" information about the excitation function. While a comparison based on the theoretical results (solid line in Fig. 3a) might suggest that the theoretical reaction cross section is markedly lower than the experimental value, averaging the theoretical excitation function over the experimental reagents' translational energy distribution leads to a value of about 0.08 $Å^2$ (filled square in Fig. 3a).

In the case of the H/D product branching ratio, averaging the theoretical $\Gamma_{\rm H/D}$ curve (solid line in Fig. 3b) over the experimental reagents' translational energy distribution leads to a value of $\Gamma_{\rm H/D} \approx 0.9$ (depicted as the filled square in Fig. 3b), which is also slightly lower than the measured value of $\Gamma_{\rm H/D} = (1.2 \pm 0.2)$.

At this point it should be noted that in the present dynamics experiment the OH radicals are rotationally excited with an average rotational angular momentum of $j_{OH} \approx 7$ [31] and the HD reagent internal quantum state distribution is a room temperature Boltzmann one, while in the calculations of the integral cross sections and branching ratios (calculated for total angular momentum J > 0) OH and HD have been assumed to be in the rotational ground state $j_{OH} = j_{HD} = 0$.

The influence of OH rotational excitation on the reactivity has been investigated for the SE-PES using the TD-QWP [24,33] and the QCT method [34]. Both types of calculations showed that OH rotation has only a minor influence on reactivity in the OH + $HD/H_2/D_2$ reactions, in particular, when averaged over a broad rotational state distribution. The same was found for the influence of OH rotation on the product branching ratio in the OH + HD reaction [24]. On the other hand, TD-QWP calculations on the SE-PES revealed a pronounced HD rotational state dependence of the OH + HD total reaction probability and the H and D atom product branching ratio [24]. The calculated HD state-specific reaction probabilities (see fig. 3c of Ref. [24]) clearly indicate that averaging the state-specific total reaction probabilities over a room temperature HD rotational distribution as present in the experiment would lead to a somewhat higher theoretical total reaction cross section and hence to a much better agreement with experiment.

The same HD rotational state averaging procedure, however, would give a some what lower theoretical value of the H/D product branching ratio (see Fig. 5 of Ref. [24]), leading to an even higher discrepancy between theory and experiment. Comparison of the product branching ratio $\Gamma_{\rm H/D} = (1.2 \pm 0.2)$ obtained in the present study with the values of $\Gamma_{\rm H/D} = 0.21$ and $\Gamma_{\rm H/D} = 0.35$ measured in kinetics experiments at temperatures of 250 and 298 K, respectively ¹ [18], clearly shows that the reaction mechanism changes as the collision energy increases. An H/D product branching ratio considerably smaller than unity can be attributed to tunnelling, which favours, at collision energies below the reaction threshold, the abstraction of H atoms (OH + HD \rightarrow D + HOH) over D atom abstraction (OH + HD \rightarrow H + HOD). The preference for the D atom abstraction channel observed in the present study is the first experimental indication that at higher translational energies the dynamics of reaction (2) might be influenced by reagents steric effects as proposed by Zhang and Zhang [23].

4. Conclusions

An absolute reaction cross section of $\sigma_{\rm R}(0.24)$ eV = (0.14 ± 0.05) Å² was measured for the OH + HD reaction and the branching ratio for the OH + $HD \rightarrow H + HOD (D + H_2O)$ product channels was determined to be $\Gamma_{\rm H/D} = (1.2 \pm 0.2)$. As far as the total reactive cross section is concerned, good agreement between experiment and accurate TD-QWP calculations on the Schatz-Elgersma potential can be expected after averaging the theoretical HD rotational state-specific reaction probabilities over a room-temperature HD rotational distribution as present in the experiment. The measured H/D product branching ratio which indicates a preference for the D atom abstraction channel is in qualitative agreement with the translational energy dependence of the product branching ratio predicted by theory. However, for a more quantitative comparison between experiment and theory, calculations of HD roomtemperature averaged quantities for total angular momentum J > 0 would be desirable. In addition, accurate TD-QWP studies on the newly developed Kliesch-Werner-Clary potential [22], for which the transition state geometry significantly differs from that of the Schatz-Elgersma potential, could be helpful for a better understanding of steric effects in diatom-diatom reactions.

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References

- J. Warnatz, U. Maas, R.W. Dibble, Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation (Springer, Heidelberg, 1996) and references therein.
- [2] R.P. Wayne, Chemistry of Atmospheres, 2nd ed. (Oxford University Press, Oxford, 1991) and references therein.
- [3] see e.g. M. Baer, H. Szichman, E. Rosenman, S. Hochman-Kowal and A. Persky in: Gas Phase Chemical Reaction Systems: Experiments and Models 100 Years after Max Bodenstein, Springer Series in Chemical Physics, Vol. 61, Eds. J. Wolfrum, H.-R. Volpp, R. Rannacher, J. Warnatz (Springer, Heidelberg, 1996) and references therein.
- [4] G.C. Schatz and J.M. Bowman, Annu. Rev. Phys. Chem. 46 (1995) 169 and references therein.
- [5] K. Kleinermanns, J. Wolfrum, Appl. Phys. B. 34 (1984) 5.
- [6] K. Kessler, K. Kleinermanns, Chem. Phys. Lett. 190 (1992) 145.
- [7] A. Jacobs, H.-R. Volpp, J. Wolfrum, Chem. Phys. Lett. 196 (1992) 249.
- [8] A. Jacobs, H.-R. Volpp and J. Wolfrum, 24th Symp. (Int.) on Combustion, The Combustion Institute, Pittsburgh, 1992, p. 605.
- [9] F.F. Crim, A. Sinha, M.C. Hsiao and J.D. Thoemke. in: Mode Selective Chemistry, Vol. 24, Eds. J. Jortner, R.D. Levine, B. Pulman (Kluwer Academic Publishers, Dordrecht, 1991).
- [10] A. Jacobs, H.-R. Volpp, J. Wolfrum, J. Chem. Phys. 100 (1994) 1936.
- [11] F.F. Crim, J. Phys. Chem. 100 (1996) 12725.
- [12] M.J. Bronikowski, W.R. Simpson, B. Girard, R.N. Zare, J. Chem. Phys. 95 (1991) 8647.
- [13] M.J. Bronikowski, W.R. Simpson, R.N. Zare, J. Phys. Chem. 97 (1993) 2204.
- [14] S. Koppe, T. Laurent, P.D. Naik, H.-R. Volpp, J. Wolfrum, Can. J. Chem. 72 (1994) 615.

¹ Calculated from the branching ratio k_{2a} / k_2 reported in Ref. [18] assuming that $k_2 = (k_{2a} + k_{2b})$.

- [15] R.A. Brownsword, M. Hillenkamp, T. Laurent, R.K. Vatsa, H.-R. Volpp, J. Wolfrum, Chem. Phys. Lett. 259 (1996) 375.
- [16] R.A. Brownsword, M. Hillenkamp, T. Laurent, H.-R. Volpp, J. Wolfrum, R.K. Vatsa and H.-S. Yoo, J. Phys. Chem. submitted 1997.
- [17] R. Atkinson, D.L. Baulch, R.A. Cox, R.F. Hampson, J. Kerr, J. Troe, J. Phys. Chem. Ref. Data 21 (1992) 1125.
- [18] R.K. Talukdar, T. Gierczak, L. Goldfarb, Y. Rudich, B.S. Madhava Rao, A.R. Ravishankara, J. Phys. Chem. 100 (1996) 3037.
- [19] J.V. Michael, in: Advances in Chemical Kinetics and Dynamics, ed. J.R. Barker (JAI Press Inc., Greenwich, 1992).
- [20] M. Alagia, N. Balucani, P. Casavecchia, D. Stranges, G.G. Volpi, J. Chem. Phys. 98 (1993) 2459.
- [21] C.B. Moore, I.W.M. Smith, J. Phys. Chem. 100 (1996) 12848.
- [22] M. Alagia, N. Balucani, P. Casavecchia, D. Stranges, G.G. Volpi, D.C. Clary, A. Kliesch, H.-J. Werner, Chem. Phys. 207 (1996) 389.
- [23] D.H. Zhang, J.Z.H. Zhang, Chem. Phys. Lett. 232 (1995) 370.

- [24] D.H. Zhang, J.Z.H. Zhang, Y. Zhang, D. Wang, Q. Zhang, J. Chem. Phys. 102 (1995) 7400.
- [25] G.C. Schatz, H. Elgersma, Chem. Phys. Lett. 73 (1980) 21.
- [26] S.P. Walch, T.H. Dunning, J. Chem. Phys. 72 (1980) 1303.
- [27] T. Laurent, P.D. Naik, H.-R. Volpp, J. Wolfrum, T. Arusi-Parpar, I. Bar, S. Rosenwaks, Chem. Phys. Lett. 236 (1995) 343.
- [28] R.A. Brownsword, M. Hillenkamp, P. Schmiechen and H.-R. Volpp (to be published).
- [29] G. Hilber, A. Lago, R. Wallenstein, J. Opt. Soc. Am. B. 4 (1987) 1753.
- [30] W.J. van der Zande, R. Zhang, R.N. Zare, K.G. McKendrick, J.J. Valentini, J. Phys. Chem. 95 (1991) 8206.
- [31] S. Koppe, T. Laurent, P.D. Naik, H.-R. Volpp and J. Wolfrum, 26th Symposium (Int.) on Combustion, The Combustion Institute, 1996, p. 489.
- [32] S. Koppe, T. Laurent, P.D. Naik, H.-R. Volpp, J. Wolfrum, T. Arusi-Parpar, I. Bar, S. Rosenwaks, Chem. Phys. Lett. 214 (1993) 546.
- [33] D.H. Zhang, J.Z.H. Zhang, J. Chem. Phys. 100 (1994) 2697.
- [34] G.C. Schatz, J. Chem. Phys. 74 (1981) 1133.