

LETTERS TO THE EDITOR

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COMMUNICATIONS

Bond-specific chemistry: OD:OH product ratios for the reactions $H+HOD(100)$ and $H+HOD(001)$

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(Received 10 September 1991; accepted 19 September 1991)

An intriguing question is whether polyatomic molecules can be prepared by vibrational excitation so that only specific parts of the molecule react.¹ Three factors conspire against such behavior in general: (1) the difficulty of preparing a molecule in a selected vibrational level; (2) the time scale that vibrational energy remains localized in a well-defined motion (vibrational mode) once the molecule is excited; and (3) the efficacy with which vibrational motion of a polyatomic molecule promotes bond-specific bimolecular reaction. Past experiments have indicated that bond-specific reactions are the exception rather than the rule.¹ Recent experiments by Crim and co-workers² have shown, however, that the reactivity of the O–H bond in HOD can be greatly enhanced by excitation of HOD into a high overtone of the O–H stretch, which to a good approximation is a local mode. In these studies, the HOD molecule was initially prepared with 4 quanta of vibration in the OH stretch and allowed to react with thermal H atoms. A strong preference for formation of OD was observed with an OD:OH branching ratio of greater than 100:1. This selectivity is in agreement with theoretical predictions of Schatz, Colton, and Grant³ and of Clary.⁴ We report here the selective cleavage of either the OH or OD bond of HOD in the reaction



when the HOD is prepared with one quantum of vibrational excitation in the selected bond. This study demonstrates that enhancement in reactivity of the excited bond is preserved for the lowest level of excitation in HOD, and this enhancement can be observed for either bond in the HOD molecule.

Our experiment is carried out in a flowing mixture of HI, H₂O, HOD, and D₂O in the ratio of 5:1:2:1, which is maintained at a total pressure of 50 mTorr. The O–H and O–D stretches of HOD are well-defined local-mode vibrational eigenstates even at the level of one quantum of excitation.^{5,6} This allows either vibration to be independently excited with the excitation retained in the vibration from the time of preparation to the time of collision. We excite HOD with one quantum of vibration in either the

O–H stretch mode HOD(001), at $\sim 3800 \text{ cm}^{-1}$, or the O–D stretch mode HOD(100), at $\sim 2800 \text{ cm}^{-1}$, using a tunable Nd:YAG-pumped optical parametric oscillator (OPO).⁷ Fast H atoms are generated by photolysis of HI at 266 nm, using the fourth harmonic of a Nd:YAG laser. Because of the two possible spin-orbit states of the resulting I atom, $I(^2P_{3/2})$ and $I(^2P_{1/2})$, the translational energies of the H atom (in the H–HOD center-of-mass frame) are 1.5 and 0.6 eV, in the ratio 1.8:1.⁸ The photolysis beam and beam from the OPO copropagate through the reaction chamber. Following a 100 ns time delay, a third counter-propagating laser beam probes the nascent OH and OD reaction products via laser-induced fluorescence (LIF) using the $A^2\Sigma^+ - X^2\Pi$ ultraviolet band system in the spectral region of 305–315 nm. This beam is generated by frequency doubling the output of a Nd:YAG-pumped dye laser. The fluorescence is collected perpendicular to the laser beam axis through a UV bandpass filter (centered at 310 nm with 10 nm FWHM) and detected by a photomultiplier (RCA C31034). The output of the photomultiplier is digitized by a gated charge integrator, and the data is recorded by a personal computer. The total pressure and the pump-probe delay are chosen to assure single-collision conditions: The product rotational distributions are invariant for time delays shorter than 200 ns at a total pressure of 50 mTorr.

Reaction (1) is endothermic by 0.66 eV (5320 cm^{-1})⁹ and has an estimated barrier of 0.94 eV (7580 cm^{-1}).¹⁰ The change in zero point energy between (1a) and (1b) is small ($\sim 40 \text{ cm}^{-1}$).¹¹ Thus the 1.5 eV H atoms have sufficient energy to react with both vibrationally excited and ground state HOD, as well as H₂O and D₂O. (The reaction of fast H atoms with ground state H₂O has been studied previously by Kleinermanns and Wolfrum¹²). The signal arising from reaction with the vibrationally excited HOD is separated from that of other reactants using a shot-by-shot subtraction procedure.⁷ Both photolysis and probe lasers operate at a repetition rate of 20 Hz while the OPO runs at 10 Hz. By scanning slowly over OH and OD lines and subtracting LIF signals from alternate probe laser shots, we are able to remove background OH and OD signals not resulting from reaction of H atoms with vibrationally excited HOD.

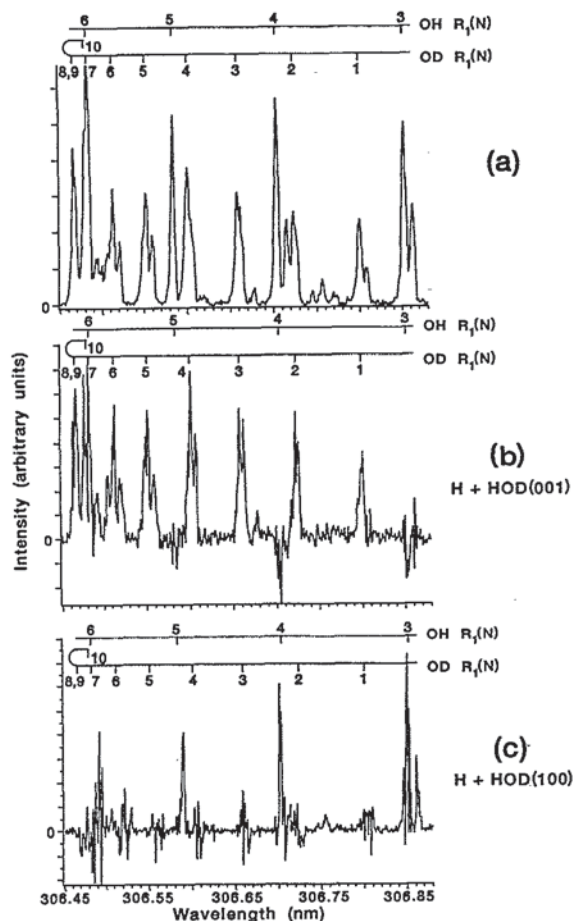


FIG. 1. Segments of OH $A-X$ and OD $A-X$ LIF excitation spectra showing the hydroxyl product for the reactions: (a) H + 1:2:1 mix of H_2O , HOD, D_2O ; (b) H + HOD(001); and (c) H + HOD(100). The assignments of the R_1 -branch lines of the OH(0,0) and OD(0,0) bands are indicated.

Figure 1 shows LIF excitation spectra of OH and OD products resulting from the reaction of translationally hot H atoms with (a) the 1:2:1 ground state mix of H_2O , HOD, and D_2O , (b) HOD excited with one quantum of O-H stretch, and (c) HOD excited with one quantum of O-D stretch. The spectra shown in Figs. 1(b) and 1(c) are obtained using shot-by-shot subtraction. We observe that to within our signal-to-noise level, the reaction of fast H atoms with HOD(001) yields exclusively OD products [Fig. 1(b)] whereas the reaction of fast H atoms with HOD(100) yields exclusively OH products [Fig. 1(c)]. (Points of negative intensity, resulting from the subtraction procedure, disappear upon averaging over many scans.) By integrating multiple scans of such spectra we find limits on the product branching ratios,

$$\text{OD:OH} > 25:1 \quad \text{for H + HOD(001)} \quad (2a)$$

and

$$\text{OD:OH} < 1:8 \quad \text{for H + HOD(100)}. \quad (2b)$$

Note that the higher limit on the ratio of (2a) simply reflects the higher signal-to-noise ratio for this experiment, which can be attributed to the larger OPO conversion ef-

iciency at 3800 cm^{-1} ($2.65 \mu\text{m}$) than at 2800 cm^{-1} ($3.57 \mu\text{m}$). The difference in limits on the branching ratio does not necessarily imply a higher degree of bond-specific selectivity.

Integrated signal intensity in Fig. 1(b) is about 25% of the intensity in Fig. 1(a). As at most only a few percent of the HOD molecules are excited by the OPO, this means that the reaction cross section is strongly enhanced by vibrational excitation of the OH bond in HOD. In the case of H + HOD(100) [Fig. 1(c)] the intensity is about 5% of that in Fig. 1(a). Because of the lower OPO conversion efficiency, it is not clear at this time to what extent OD bond excitation in HOD changes the reaction cross section.

The present study demonstrates that even at low levels of vibrational excitation we can selectively break a chosen bond in a polyatomic molecule by exciting a mode that causes this bond to be extended. We believe that this result may be general; it should be possible to achieve bond-selective chemistry in reactions of polyatomic molecules satisfying three criteria: individual modes can be pumped, vibrational excitation remains localized until a collision occurs, and the collision leading to reaction does not randomize the energy.

We thank Rong Zhang for much valuable technical advice in the course of these experiments. M.J.B. gratefully acknowledges a GAANN graduate fellowship from the U. S. Department of Education. W. R. S. thanks the National Science Foundation for a graduate fellowship. B. G. thanks NATO and CNRS for postdoctoral fellowship support. This work was supported by the National Science Foundation under Grant No. CHE 89-21198.

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