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Stereodynamical Origin of Anti-Arrhenius Kinetics: Negative Activation Energy and Roaming for a Four-Atom Reaction

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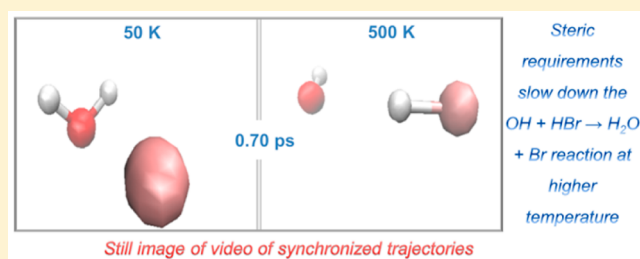
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Supporting Information

ABSTRACT: The $\text{OH} + \text{HBr} \rightarrow \text{H}_2\text{O} + \text{Br}$ reaction, prototypical of halogen-atom liberating processes relevant to mechanisms for atmospheric ozone destruction, attracted frequent attention of experimental chemical kinetics: the nature of the unusual reactivity drop from low to high temperatures eluded a variety of theoretical efforts, ranking this one among the most studied four-atom reactions. Here, inspired by oriented molecular-beams experiments, we develop a first-principles stereodynamical approach. Thermalized sets of trajectories, evolving on a multidimensional potential energy surface quantum mechanically generated on-the-fly, provide a map of most visited regions at each temperature. Visualizations of rearrangements of bonds along trajectories and of the role of specific angles of reactants' mutual approach elucidate the mechanistic change from the low kinetic energy regime (where incident reactants reorient to find the propitious alignment leading to reaction) to high temperature (where speed hinders adjustment of directionality and roaming delays reactivity).



The reaction $\text{OH} + \text{HBr} \rightarrow \text{H}_2\text{O} + \text{Br}$ is considered as a benchmark elementary process that exhibits negative temperature dependence of the reaction rate^{1–7} (anti-Arrhenius behavior). Recently, quantum chemical calculations of an accurate global potential energy surface⁸ and extensive classical trajectory simulations⁹ reproduced the behavior, whereas a review¹⁰ pointed out at existing evidence from molecular beam scattering experiments with oriented reactants^{11,12} of the key role of stereodynamics, establishing the ground for a mechanistic interpretation.

This reaction is of relevance in atmospheric modeling because it belongs to a class of processes producing halogen atoms that are destroyers of ozone.¹³ At thermal energies, it proceeds through a negligible barrier and its cross section decreases as the collision energy increases.^{14,15} From a theoretical viewpoint, this observed negative collision energy dependence could not be explained by the average long-range dipole–dipole attraction between the reactants; we argue that a relevant molecular reorientation occurs and the effect becomes less pronounced as the collision energy increases and reactants have less time to rotate toward the reactive direction. This paper reports numerical experiments to document this effect.

Motivations and background information are illustrated with reference to Figure 1. Left panels define the geometrical

parameters for the configuration of this four-atom system; the reaction profile is drawn according to recent accurate quantum chemical calculations:⁸ the van der Waals-type entrance channel well leads to a transition state at lower an energy than that of the reagents. Cross section data are from crossed beam experiments^{14,15} and show a dramatic drop as a function of collision energy; stereodynamical information is also provided^{11,12} on role of mutual direction of approaching reactants: a relevant angle θ , also defined in the figure, serves to discuss the effect. On the right, we present an Arrhenius plot for a selection of available experimental rate constants^{1–7} showing the unusual temperature dependence fitted by the d -Arrhenius formula recently introduced^{16–19} for sub- and super-Arrhenius cases, and here extended to anti-Arrhenius behavior (see Supporting Information). The addition of the parameter d accounts for deviations from linearity of the plot. The apparent activation energy, E_a , is extracted and seen to be temperature dependent and negative.

The strategy that we follow is to use the Born–Oppenheimer molecular dynamics (BOMD)^{20,21} approach to visualize the

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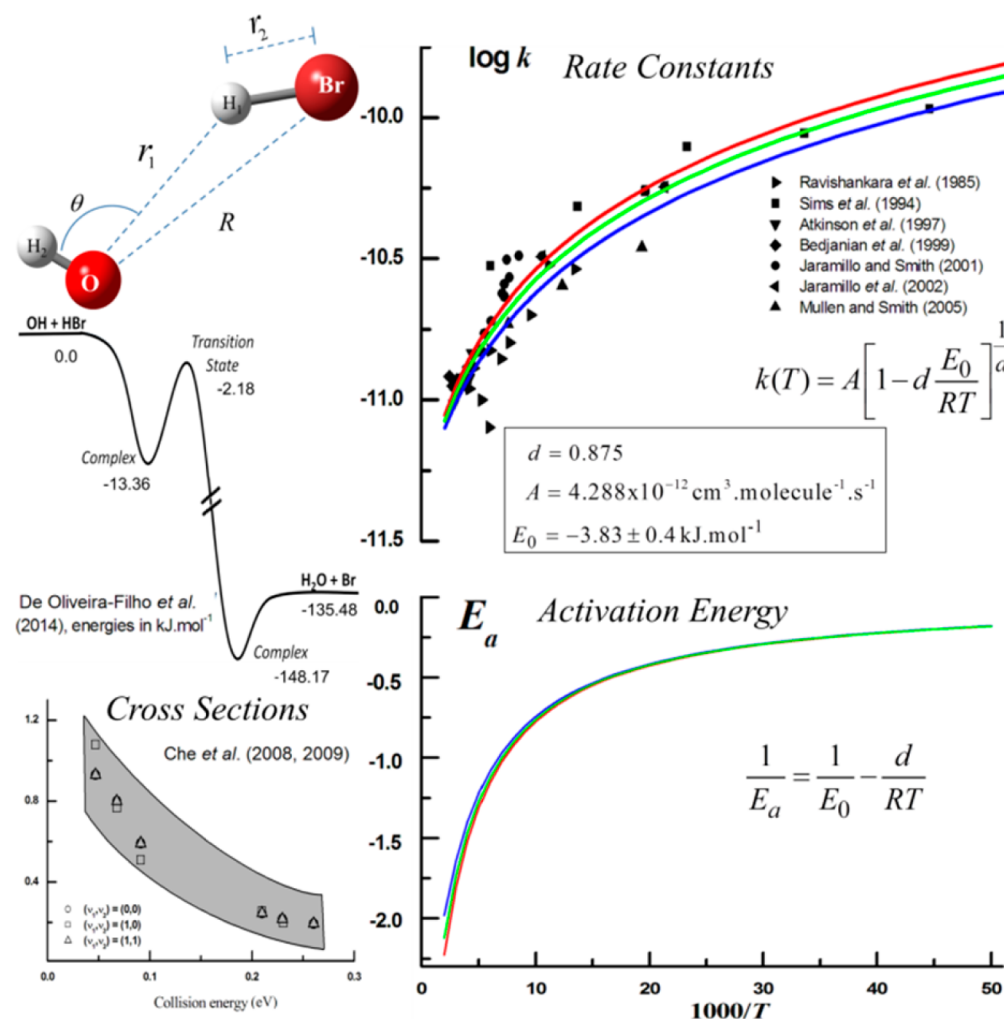


Figure 1. Coordinates, energy profile, cross sections for specific vibrational states of product H_2O , Arrhenius plots of rate constants and temperature dependence of activation energy. To give a view of the general trend, we show a fit of selected kinetic data with the d -Arrhenius formula describing curvatures in Arrhenius plots.^{16–19} The central curves correspond to the best fit for E_0 , the others show those corresponding to its estimated limiting values.

reaction in a box, our “nanoreactor” in the spirit of ref 22, whereby the system explores the potential energy surface at a specified temperature, simulated by a Nosé–Hoover thermalizing bath.²³ Although computations of the potential energy surface on-the-fly are time-consuming, we can scrutinize trajectories at different configurations and will examine comparatively their behavior at two extreme temperatures, according to this sequence: (i) by having a global look to obtain information on selective sensitivity to the features of the free energy surface when explored at slow or fast speed; (ii) by focusing on three exemplarily selected trajectories to follow in time rupture and formation of bonds; (iii) by showing how trajectories exhibit molecular reorientation for favorable reactivity, and document interesting manifestations of the roaming phenomenon and of the crucial role of stereodynamics. A movie showing the synchronized progress of two trajectories with the same initial configurations at two given temperature contributes to the visualization of these concepts (see the video in Supporting Information).

Anti-Arrhenius Behavior and Negative Activation Energy. For this four-atom system, archetypal of four-center reactions: (i) accurate computation and fitting of six-dimensional PES is demanding, (ii) exact quantum close coupling state-to-state

dynamics is prohibitively expensive, and (iii) even for reduced dimensionality models benchmark cross sections are difficult to obtain and rate constants out-of-reach. Although this reaction involves hydrogen exchange, tunneling is arguably not influential, according to deuterium substitution experiments⁵ and the accepted reaction profile⁸ (see Figure 1). The latter is a cut of a recent potential energy surface on which classical trajectory calculations⁹ of reaction rates provided agreement with the temperature dependent experimental data. The unusual barrier at an energy lower than that of reactants arising from the pronounced van der Waals well for the approaching reactants is pointed out as important for the apparent negative activation energy. However, the authors do not discuss any role of stereodynamics in favoring low temperature reactivity and disfavoring high-temperature reactive outcomes.

The importance of stereodynamical aspects had been convincingly revealed in experiments, where in order to understand orientational effects, the Osaka group^{11,12,14,15} studied this reaction using crossed molecular beams for higher than thermal energy (0.05–0.26 eV): the results indicated that the cross section decreases, increasing the collision energy (Figure 1) and suggest that reorientation effects of the reagents

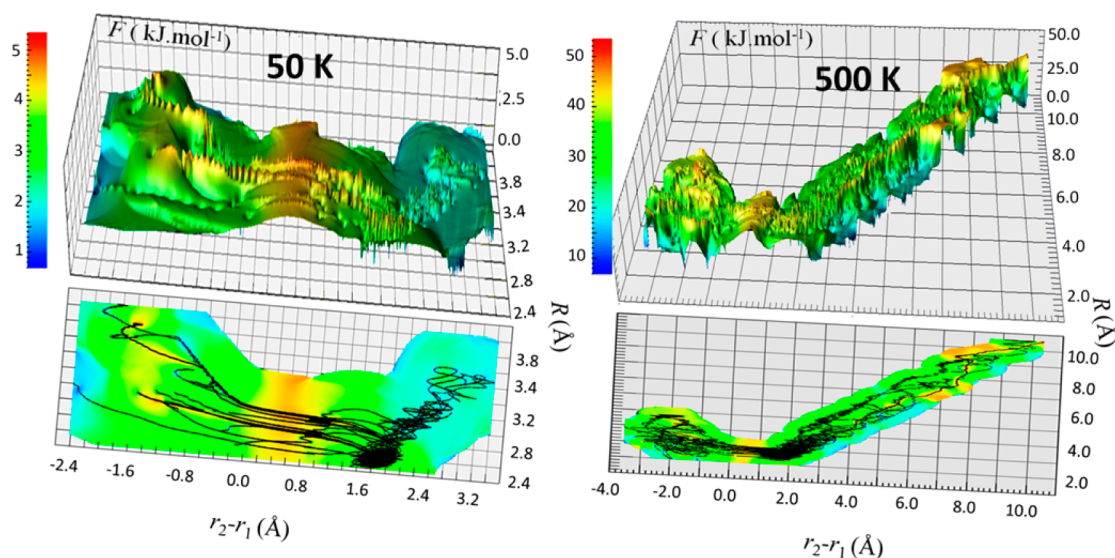


Figure 2. “Canonical” trajectories in the reactive box: reconstruction of free energy surfaces as sampled by several trajectories at low (50 K, left panels) and high (500 K, right panels) temperatures.

strongly favor the reactivity. To test the energy dependence of reorientation effects and to extract information on the relative reactivity of the O-end, H-end, and sideways collisions, the Osaka group used an orienting hexapole electrostatic field. Regarding the relative importance of the reactive sites, it was found that the O-end attack is most favored for this reaction than that of H-end attack by a factor 3.4 ± 2.3 ; they also suggested a cone of acceptance with a limiting angle¹¹ of $\alpha = 117 \pm 13$ degrees for the reaction to occur (their $\alpha = \pi - \theta$, where θ is defined in Figure 1). Our results provide a theoretical framework for this effect confirming the experimentally derived suggestion that the negative temperature dependence of the $\text{OH} + \text{HBr}$ has a stereodynamical origin, overlooked by previous theoretical studies.

First-Principles Approach. First-principles molecular dynamics is presented here for the first time for this prototypical halogen generating reaction. For a pioneering investigation of a reaction involving an OH radical, see ref 24, where Car–Parrinello dynamics was used. However, with respect to the original Car–Parrinello type of approaches, where motion of the nuclei in the on-the-fly dynamics occurs in the potential generated by the electrons and governed by classical mechanics, the wave functions here are converged at every step, making trajectory calculations much more expensive but arguably more accurate.²¹

Interatomic forces are not preassigned but are obtained through electronic structure calculations, and chemical reactions occur as the electronic structure adjusts to the evolving atomic positions. In this way, it is possible to determine reaction mechanisms with no reference to previously determined reaction pathways. Rather, the exploit of the automatic focusing of trajectories on regions actually sampled during the process provides information on parts of the multidimensional potential energy surface that demand more accuracy for realistic simulations of the dynamics. Randomly generated initial conditions and procedures for equilibration with respect to thermal baths (see details in Supporting Information) permit to efficiently bypass the often severe bottlenecks of computational dynamics, such as both the impact parameter integration to provide total cross sections,

and their Boltzmann kinetic energy averaging; this allows us to directly express results at a specific temperature: our choice was to consider two extremes of the experimentally relevant range, at low (50 K) and high (500 K) temperatures.

Figure 2 is an overview of results for trajectories within the reactive box. We define these trajectories as “canonical” being intended as evolving at given temperatures²³ (those trajectories found as nonreactive were stored for further analysis): the reconstruction of free energy surfaces (upper panels) as sampled by several trajectories is shown at low and high temperatures: although arguably valid within a close neighborhood, the graphical extension is intended to visually help the readers’ perception. A table in Supporting Information lists the initial configurations of the trajectories that are reported but not distinguishable in Figure 2: they will be discussed in detail later. The horizontal coordinate is the difference between lengths of the bond that is progressively broken r_2 and of the one which is concertedly formed r_1 (Figure 1). The transverse coordinate R , the length of the bond between O and Br, can be regarded as approximately proportional either to the principal moment of inertia of this nearly oblate top system or else to the hyperradius of the hyperspherical approach. The lower panels show the bunch of the reactive trajectories on the R , $r_2 - r_1$ plane (the identification of each of them with the corresponding initial conditions listed in the Table of Supporting Information is not attempted here but is discussed graphically in the following).

At low temperature, all reactive trajectories are seen to enter the box in the upper left corner and evolve, whereas the R coordinate attains a range of minimum values in the closest approach configurations, where the $r_2 - r_1$ coordinate changes sign; then they continue downhill (the vibrational excitation of the newly formed bond appears as wavelets in the graph) until they exit the box toward product formation in the lower right corner of the figure. The free energy landscape from left to right shows an early stage, exhibiting a decreasing tendency to a small basin due to the intermolecular attraction between the reactants, then the ascent to a barrier, followed by the fall into the basin of the intermolecular interactions between the incipiently departing products. Eventually, they separate with

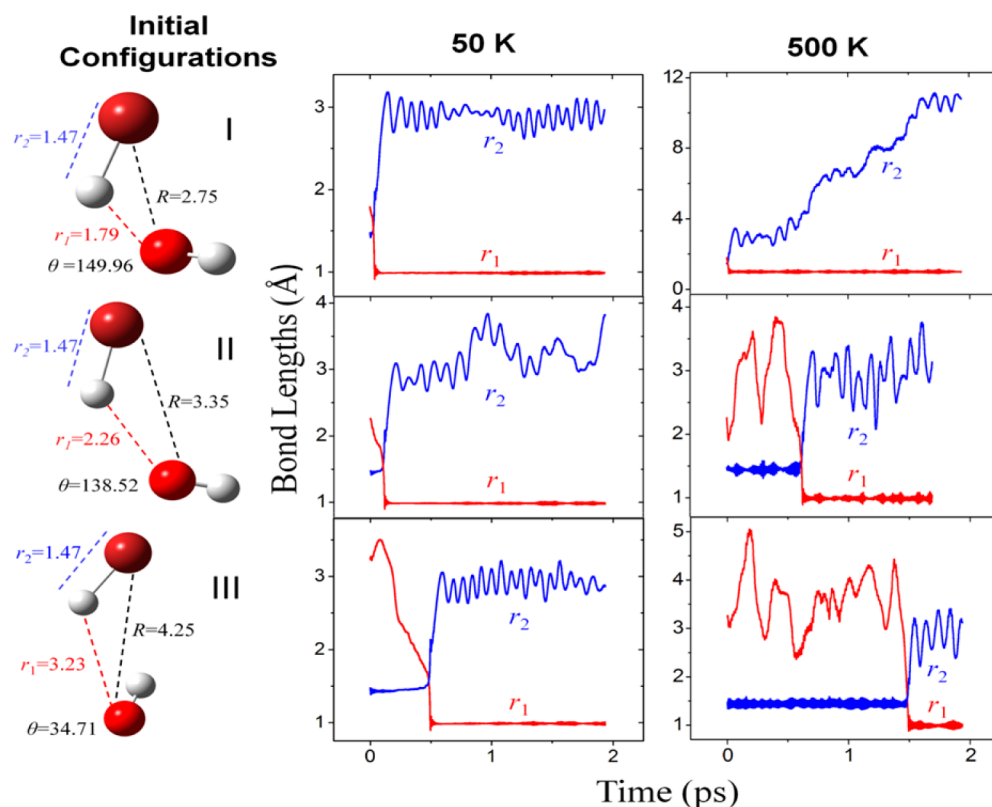


Figure 3. Exemplary “canonical” trajectories at two temperatures for three initial configurations I, II and III, chosen among those that are found to lead to reaction. Estimated switching times (in picoseconds) are, respectively: 0.05, 0.11, 0.50 at 50 K and 0.01, 0.64, 1.50 at 500 K.

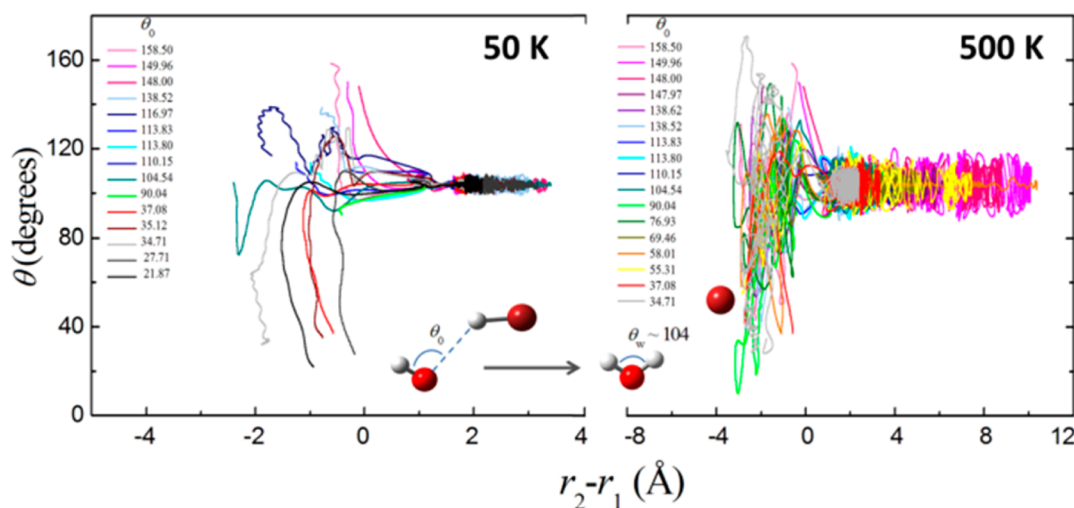


Figure 4. Evolution at two temperatures of the stereodynamical angle of approach θ defined in Figure 1 for “canonical” trajectories (see Table in Supporting Information). Colors indicate the initial value of θ , denoted by θ_0 .

large vibrational energy in the newly formed bond of the water molecule. This progression is a manifestation of the minimum energy path profile for this exothermic reaction (Figure 1), characterized by van der Waals-like complexes in the reactant and product channels and by a transition-state barrier energetically lower than the entrance channel.

At high temperature, reactive trajectories are seen that, after entering the box from different directions, only subsequently find their relatively narrow way toward product formation, and are much less sensitive to the details of the reaction profile.

Delayed Reactivity and Roaming. The three initial configurations shown in Figure 3, correspond to the given geometrical parameters (see also Table in Supporting Information); the lengths of the bond that is broken r_2 and of the bond that is formed r_1 are reported as a function of time. After hydrogen exchange, the interatomic distance r_1 is seen tending fast to the asymptotic value ca. 1 Å that correspond to the length of the OH bond of water, with some vibrational stretching at 500 K. For I, where reactants enter the reactive box with a favorable configuration, reaction occurs suddenly. For II and III, where the dynamics is started with increasingly larger initial

elongation for r_1 , reaction is delayed, and roaming in the entrance channel manifests with ample oscillations. Initial values for R and θ similarly contribute, and the effect is dramatically enhanced at high temperature, where interesting signatures of “roaming” also are particularly evident as increasingly ample vibrations of the bond being broken, whereas bromine tends to move away.

For the following discussion, interesting is the “switching” time, occurring when along trajectories, $r_1 = r_2$, that to a very rough approximation can be considered as the moment that reaction occurs. The main visual impression (see also the video in Supporting Information) is the evident delayed reactivity for trajectories in the search of encountering proper paths, a phenomenon that is impeded at high temperature. More pronounced is also seen the apparent “roaming” in vibrational modes in search of favorable outcomes when initial r_1 is stretched, to be contrasted for example to the round-about mechanism seen in S_N2 reaction dynamics.²⁵

The “roaming” effect can often be attributed to the manifestation of nonadiabatic transitions and has been individuated and documented as the occurrence in photodissociation experiments of alternative routes to molecular fragmentation channels^{26,27} that avoid passing through the transition state. The presence of these alternative pathways can be inferred by the properties of the energy distribution of the product fragments and indicates that attention be devoted to regions of the potential energy surfaces other than those in the neighborhoods of saddle points along minimum energy paths: eventually this leads to discovery avenues to reaction beyond the venerable transition state theory approach.^{10,27}

The origin of roaming as a rearrangement between weakly bound reactants is connected to high-lying reaction channels.²⁸ In refs 29 and 30, observed roaming was perputed by pronounced bond elongation in methyl formate²⁹ emerging from a conical intersection: similarly, in the present case, it is favored by trajectories originating at elongated r_1 . However, exothermicity appears not to be used for appreciable vibrational excitation of the formed bond.

Stereodynamics and Excitation of Bending for the Water Product. Figure 4 provides documentation of the role of stereodynamics in the peculiar kinetics of this reaction. The “canonical” reactive trajectories, as a function of the variable $r_2 - r_1$, are distinguished by different colors as listed and arranged in decreasing order of θ_0 , the initial values for the θ angle (the other parameters characterizing the initial configurations are reported in the Table in Supporting Information). The figure shows that when the dynamics is started with those values of θ_0 close to that directly leading to the formation of the bending angle of water, the system finds an easier way to products, and possible reorientation facilitating the process is impeded at high temperature. Note again the “roaming” effect as the search of a favorable approaching angle for reactivity (see video in Supporting Information).

Remarkably, substantial energy appears to dispose as excitation in the bending mode of the product water, as it is visually clear to a much greater extent for the higher temperature (see ref 31 for experimental comparisons). The range of values of the θ angle can be analyzed in terms of the energy disposal into the bending mode.

In retrospect, results from this paper describing reactivity in a four-atom system are insightful in view of the enormous difficulties that are encountered to provide theoretically benchmark rate constants. Great effort is needed to go all the

way from the intermolecular interactions to rate constants, through state-to-state coupled-channel Schrödinger dynamics (to obtain scattering matrices), followed by sums over angular momenta (to obtain differential and integral cross sections) and finally by Boltzmann averaging to obtain the rates. Only recently, this has been achieved for a triatomic system and predictions³² have been verified experimentally for very low temperature reactivity.³³ However, comparison of results for this four-atom reaction with related three-atom processes is interesting: de Oliveira-Filho et al.⁹ commented on the reaction $O + HBr$; in addition, we indicate as insightful to consider also the $H + HBr$ reaction, for which Pomerantz et al.³⁴ gave experimental and computational evidence of reactive trajectories far from minimum energy path, an unnoticed signature of “roaming” in the sense of our discussion of Figure 3.

The involved computational effort forced us to limit the number of trajectories and thus the statistical validity of our sampling. However, we did not present here very numerous nonreactive events: the data are stored and available for future analysis within an extension of this work to more quantitative investigations, which are in progress for this and other reactions of analogous complexity. Nevertheless an order-of-magnitude estimate of rates can be of interest: in our numerical experiments, we place one molecule of both OH and HBr in a cubic box of 6 Å in size under periodic boundary conditions, amounting to a concentration of $\sim 3 \times 10^{21}$ molecules cm^{-3} for each reactant. From the decay times of the order of 1 ps at 50 K and 2 ps at 500 K, one estimates bimolecular rates of order $\sim 3 \times 10^{-11}$ and 1.5×10^{-11} cm^3 molecules⁻¹ s⁻¹, respectively, in a range compatible with experimental values (Figure 1).

■ ASSOCIATED CONTENT

● Supporting Information

Details of the theoretical and computational methods. Movie (MOV format) with synchronized trajectories of the OH + HBr reaction at low and high temperatures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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