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The Reaction between Sodium Hydroxide and Atomic Hydrogen in Atmospheric and Flame Chemistry

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Supplementary Information

Classical trajectory simulations were employed to obtain insight into the NaOH + H collision dynamics. The simulations were carried out using the Born-Oppenheimer Molecular Dynamics (BOMD) method[1, 2] at the MP2-B3LYP/6-311+G(2d,p)level of theory[3] as implemented in the Gaussian 09 suite of programs.[3] Over 700 trajectories were run at a single collision energy, namely $k_B T$ at T = 300 K, and with NaOH initially at its linear equilibrium geometry (r_{NaO} = 1.975 Å; r_{OH} = 0.957 Å). The BOMD trajectory steps used fully converged self-consistent field (SCF) results.

Other than the collision energy, three parameters were used to specify the initial conditions for each trajectory. The first parameter was α_0, the angle between $\mathbf{v}_0$ and $\mathbf{r}_0$, the vectors specifying the initial relative velocity of the reactants ($\mathbf{v}_0$) and the initial orientation of the Na-O-H axis ($\mathbf{r}_0$). The former was taken to point from H to the center of mass of NaOH, the latter from the H end to the Na end of NaOH. We used five different values for α_0. The values described head-on H attack of either end of the NaOH molecule ($\alpha_0 = 0$ or 180°), side-on attack ($\alpha_0 = 90^{\circ}$), and intermediate arrangements ($\alpha_0 = 45^{\circ}$ or 135°).

The second parameter used to specify initial conditions was y_0, the distance between $\mathbf{r}_0$ and the plane, parallel to $\mathbf{r}_0$, containing $\mathbf{v}_0$. The y_0 parameter determined how off-center was the initial H-NaOH approach. It was varied from 0 to values large enough for the H-NaOH interaction to become entirely negligible.

The third initial conditions parameter, x_0, was needed only when the initial attack was not head-on (i.e., with $\alpha_0 = 45^{\circ}$, 90°, or 135°). It specified the initial target point —the point where the incoming atom would come closest to $\mathbf{r}_0$, or cross it, if there were no atom-molecule interactions. It was varied from values between the Na-end and the H-end of NaOH to values beyond the NaOH ends that were far enough for the H-NaOH interaction to become entirely negligible.

Figure S1 summarizes the important results of our simulations. It indicates the initial positions of the Na, O, and H atoms of NaOH (large circles filled with a dotted pattern) and covers a region where the H-NaOH interaction is far from negligible (x_0, horizontal, up to 3 Å beyond either end of NaOH; y_0, vertical, up to 4 Å). The horizontal arrows indicate head-on attack at either end of NaOH and with different y_0 values; the colour indicates whether the trajectory resulted in reaction (black) or not (gray). The small circles indicate other attack directions (with $\alpha_0 = 45^{\circ}$, 90°, or 135°); open circles indicate that none of the three trajectories resulted in reaction, whereas solid black circles indicate that at least one of the three trajectories did lead a to chemical reaction. The gray shading indicates the region where we found that reaction could possibly occur; note that in includes all of the solid black circles (i.e., all combinations of x_0 and y_0 associated with at least one reactive trajectory).

As indicated on Fig. S1, we found that head-on attack — in other terms, collinear collision geometries — is not conducive to reactivity. Indeed, only one of the trajectories involving head-on attack (not all are shown on Fig. S1) was found to result in reaction. This is consistent with the fact that, unless significantly off-centre, collinear approach leads to an energy barrier (see Fig. 4 of the article) and H-NaOH repulsion. In the one trajectory that did lead to reaction (see Movie 1), the y_0 value is “just right” (at the collision energy used in our simulations) to allow for capture of the incoming H atom in the potential energy well perpendicular to the NaOH axis (see Fig. 4 of the article). The other collinear collisions have led either to H rebound from the repulsive potential near the NaOH ends or to deflection without capture.

The comments above suggest that reactivity should increase for side-on collisions. Our simulations provided further evidence for this, but also revealed the following. First, that side-on or approximately side-on attack is not strongly conducive to reaction. We found that capture of the incoming H atom is a necessary step for reaction; when the visit of the incoming atom to the energy well was brief, involving a succession of bounces off its outer walls but no proximity to the Na-O axis, the trajectory turned out to be inelastic. H atom capture being subject to significant steric hindrance, reactivity is low.

Another interesting observation was that H atom capture leads to an H-NaOH complex with high vibrational excitation. This complex can be very long lived, but it is very unlikely to break into NaOH + H. None of our trajectories resulted in H-atom exchange, and in all trajectories where the H-NaOH complex was clearly formed, dissociation was into Na + H_2O, sometimes after a number of wide-amplitude Na-OH_2 vibrations (see Movie 2, in which the H-NaOH complex survives for about 2 ps, for an example). In inelastic trajectories, the H atom either rebounded quickly, or else visited only the outer parts of the potential energy well. This reinforces the idea that the aforementioned steric constraints are the main deterrents to reactivity.

For each value of α_0, the NaOH + H → Na + H_2O reaction cross section was estimated as the area of the region, in a plane transverse to $\mathbf{v}_0$ (that is, a plane perpendicular to the H-NaOH approach direction), which the incoming H atom must hit for reaction to occur. In the collinear cases, $\alpha_0 = 0$ or 180°, we found this area to be vanishingly small (see discussion above). In the other cases, the estimate started with consideration of the results in Figs. S2a–c. These figures are similar to Fig. 1, except that each of them includes results associated with a particular α_0 value (respectively, $\alpha_0 = 45°$, $\alpha_0 = 90°$, and $\alpha_0 = 135°$). In the $\alpha_0 = 90°$ case (Fig. S2b), the shaded region is already in the plane transverse to $\mathbf{v}_0$; its area, 14.7 $Å^2$, is our estimate for the reaction cross section at $\alpha_0 = 90°$. In the $\alpha_0 = 45°$and $\alpha_0 = 135°$ cases (Figs. S2a and S2c, respectively) the plane of the figure is not the plane transverse to $\mathbf{v}_0$. To estimate the corresponding reaction cross sections, the areas of the shaded regions must be multiplied by a geometric correction factor, $\gamma = \sin(45°) = \sin(135°)$. The results are 9.7 $Å^2$ for $\alpha_0 = 45°$, and 12.3 $Å^2$ for $\alpha_0 = 135°$.

Averaging over the five α_0 values, we arrive at the estimate for the reaction cross section quoted in the article: 7 $Å^2$.

References

(1) Helgaker, T.; Uggerud, E.; Jensen, H. J. A., Integration of the Classical Equations of Motion on ab initio Molecular-Potential Energy Surfaces Using Gradients and Hessians – Application to Translational Energy-Release Upon Fragmentation. Chem. Phys. Lett. **1990,** 173, 145-50.

(2) Li, X.; Millam, J. M.; Schlegel, H. B., Ab Initio Molecular Dynamics Studies of the Photodissociation of Formaldehyde, $H_2CO \rightarrow H_2 + CO$: Direct Classical Trajectory Calculations by MP2 and Density Functional Theory. J. Chem. Phys. **2000,** 113, 10062-10067.

(3) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H., et al., Gaussian 09, Revision A. 01, Gaussian. Inc., Wallingford, CT **2009**.

Figures

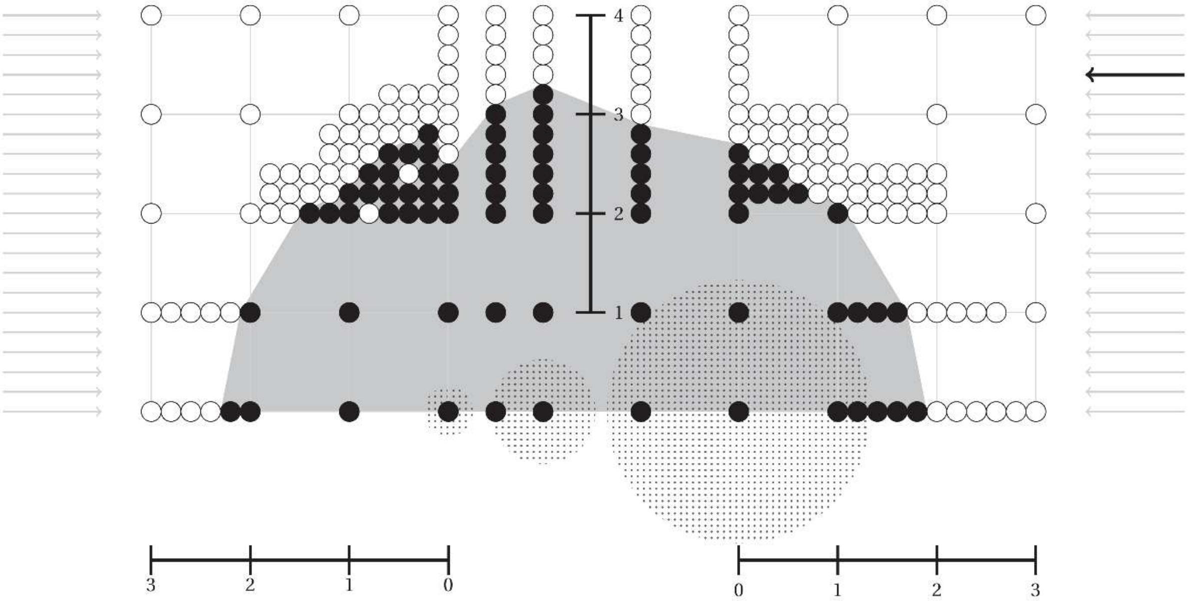

Figure S1. Schematic representation of the results of trajectory simulations. See text for details.

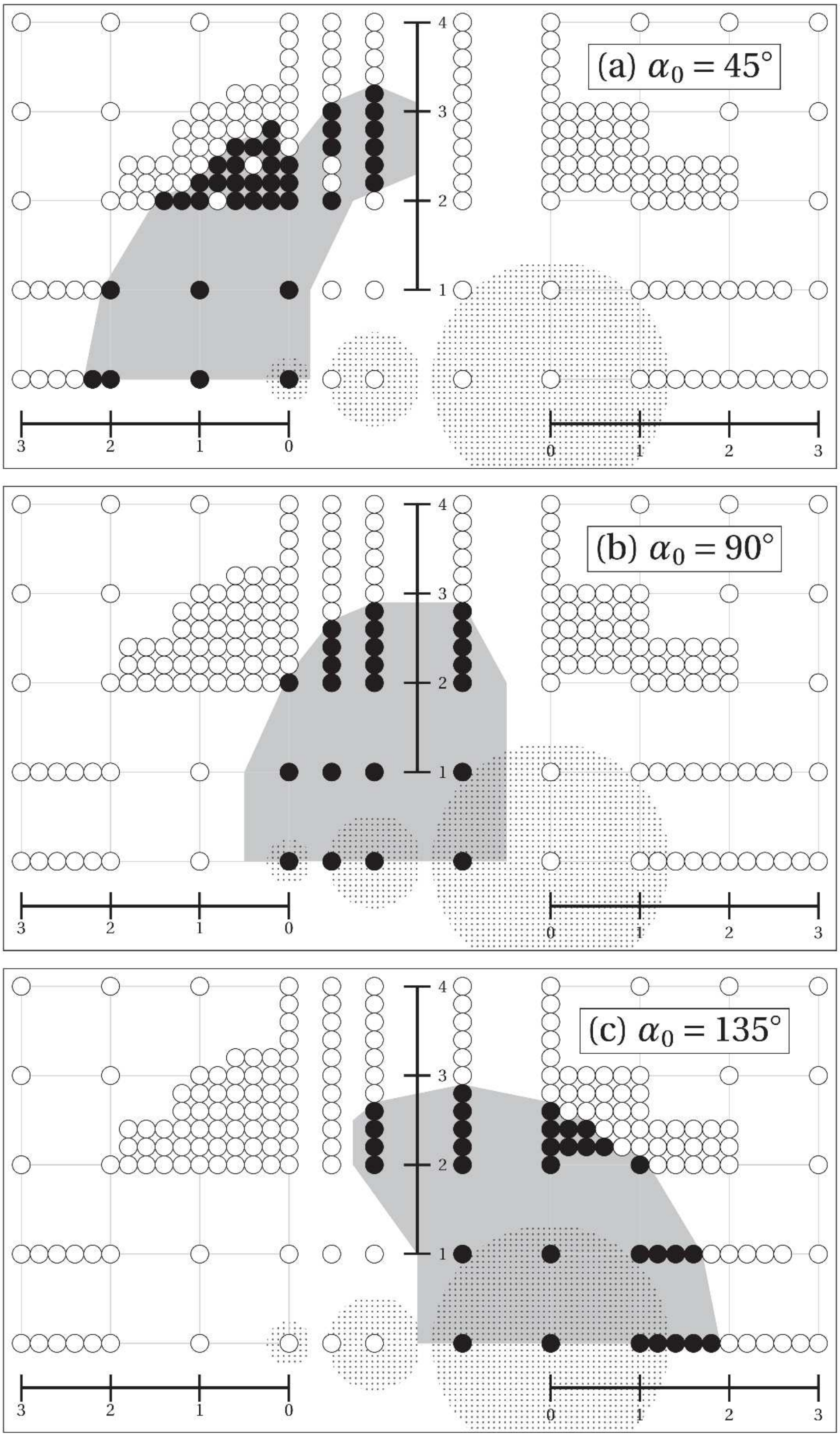

Figure S2. As Fig. S1, except that each panel shows results that follow from using a particular value for α_0, as indicated on the legend for each panel.

Animations

Movie 1. Evolution of a reactive trajectory with initial conditions as determined by $\alpha_0 =$ $\alpha_0 = 180^{\circ}$ and $y_0 = 3.4$ Å.

Movie 2. Evolution of a reactive trajectory with initial conditions as determined by $\alpha_0 =$ $\alpha_0 = 135^{\circ}$, $y_0 = 2.8$ Å and x_0 halfway between the centres of the sodium and oxygen atoms.