Stereoselectivity as a Probe of Unexpected Reaction Pathways

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For gas-phase chemical reactions like $OH + HCl \rightarrow H_2O + Cl$, which involves a relatively deep pre-barrier van der Waals well, quasi-classical trajectory calculations showed that unexpected reaction pathways involving strong reorientation of the reagents may be clearly evidenced by controlling the spatial orientation of both reagent molecules. In such a case, the venerable notion of cone of acceptance does not suffice, on its own, to rationalize steric effects.

Dynamical stereochemistry is the study of the steric effect, i.e., the dependence of the reaction cross section on the spatial orientation of the reagents.[1–3] Since the pioneering work of Bernstein, Brooks, and co-workers,[1,2,4] this research field, the main objective of which is to deepen our understanding of chemical reactivity, has become very active.[5–7]

The traditional view of the barrier crossing problem deals with the notion of the cone of acceptance or of reaction, schematically represented in Fig. 1 for the much studied reaction $Rb + CH_3I \rightarrow RbI + CH_3$. The Rb atom is directed towards point A which belongs to a portion of sphere centered on the I atom. This portion of sphere is supposed to define roughly all the configurations reachable at the barrier top, for which the potential energy V of interaction between nuclei is lower than or equal to the total energy E. Since ICH_3 is supposed here to be rovibrationally frozen, E is equal to the collision energy. Its circular contour corresponds to the turning points for which V and E are equal. Given the perspective from which the molecular system is represented, this contour has the shape of a streched ellipse. In point A in Fig. 1, the projection of the velocity v along the line of center supported by A and the iodine atom is denoted $v_\perp$. If the interaction between reagents up to the sphere is neglected, the system should react if (a) the kinetic energy $E_\perp = \mu {v_\perp}^2/2$ (μ is the reduced mass of Rb with respect to ICH_3) along the line of center at the barrier top is larger than the potential energy at the same place and (b) no recrossing of the barrier is possible, which is a quite reasonable assumption in most cases. In addition, if the potential energy barrier at the top is approximated by a simple analytical expression, it is possible to develop compact and elegant expressions of the reaction cross section and rate constant in which key steric factors appear explicitly. The previous is the main idea underpinning the angular-dependent line of center model (ADLOC) proposed by Smith[8] and Levine and Bernstein[9] in the early 80's. This model has been improved in order to take into account the possible ellipsoidal shape of the barrier top,[10–12] or its real shape.[13] The interaction before the barrier top, which may be responsible for the reorientation of the reagents before barrier crossing, has also been incorporated in the formulation in the case where reorientation is relatively small.[14,15] In its simplest version, however, the ADLOC model nicely explains why, for instance, when Rb approaches the I end of CH_3I, the reactivity is high, whereas when it approaches the methyl group, it is extremely small.[2]

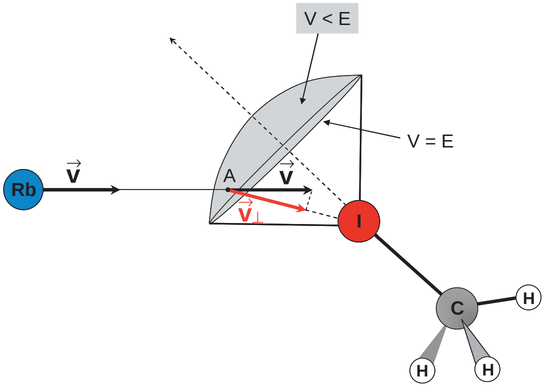

Fig. 1. Schematic representation of the cone of acceptance for the much studied reaction $Rb + CH_3I \rightarrow RbI + CH_3$.

The goal of the present note is to show that the above scenario is not sufficient, on its own, to rationalize steric effects when there is a relatively deep pre-barrier van der Waals well along the reaction path, as is the case for the reaction $OH + HCl \rightarrow H_2O + Cl$ (see Fig. 2). In such a case, reorientation may create unexpected pathways in addition to the expected ones. As shown below, stereoselectivity might be an excellent way to probe the pathways.

Simulation

In principle, stereoselectivity can be achieved in the experiment developed by some of the authors.[16] Their method is schematically represented in Fig. 3. A beam of vibrationally cold OH radicals is produced by electric discharge. Rotational state selection of the OH radicals is achieved by a 1-m hexapole field. One may for instance produce OH radicals in the

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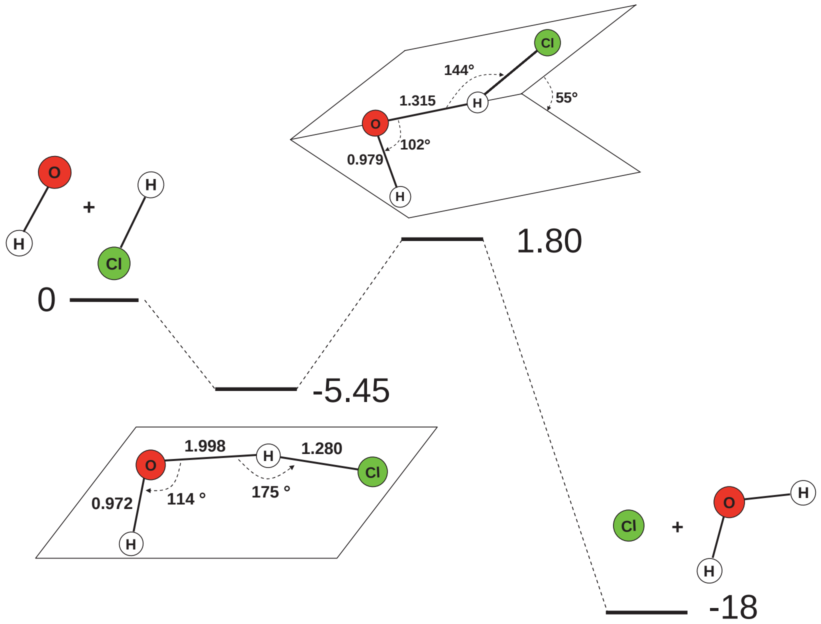

Fig. 2. Potential energy profile along the reaction path for the reaction OH + HCl → Cl + H_2O in the electronic ground state. The geometries corresponding to the pre-barrier van der Waals well (coplanar system) and the barrier top are displayed. Energies are in kcal mol^{-1} and distances are in Å.

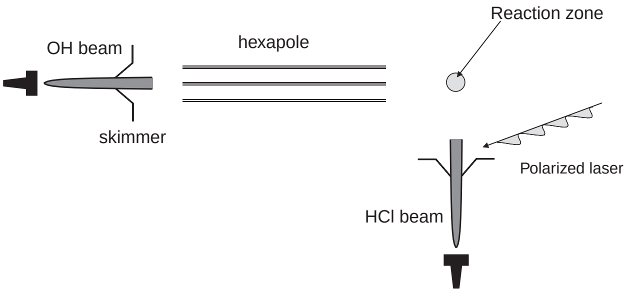

Fig. 3. Scheme of the experimental apparatus of Che and Kasai.[16]

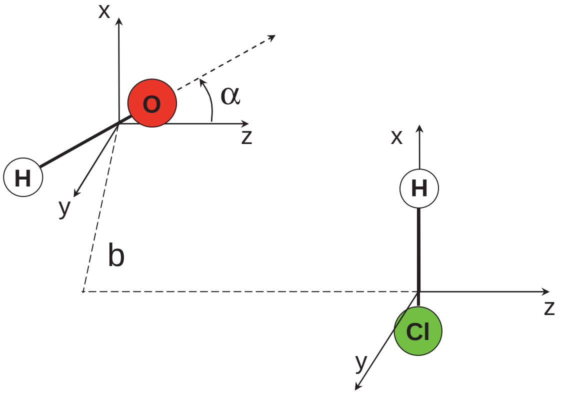

Fig. 4. Initial orientations of the diatoms. Here, HCl is aligned along the x axis but any alignment may be envisaged.

rotational ground state which are finally oriented with respect to the laboratory system in an orienting field. A beam of vibrationally cold HCl molecules, the alignment of which is selected by a polarized laser prior to the crossing point, is then crossed with the OH beam. At the laser wavelength chosen by Che and Kasai,[16] the transition dipole moment is perpendicular to the HCl axis. If the HCl beam is supersonic so that HCl is mainly in its rotational ground state, the HCl molecules that are not fragmented by photon absorption are aligned with the laser field. By varying both the orienting and laser fields and measuring the amount of Cl atoms produced by the reaction, it is possible to study the effect of spatial control of the reagents on the reactivity. The critical issue is, however, the difficulty in detecting the small amount of Cl atoms produced.

While waiting for technical problems to be overcome, we simulated this experiment by the quasi-classical trajectory (QCT) method[17] on the ab-initio potential energy surface (PES) of the electronic ground state developed by Garcia et al.[18] In the last decade or so, the QCT method has proved to provide a good overall description of the dynamics[19] provided that tunneling is negligible, which is the case for the process studied here (see below). Moreover, the reaction with the largest number of atoms that has been studied by doing exact quantum calculations, so far, is OH + H_2 → H_2O + H.[20] Contrary to the previous process, the reaction OH + HCl → H_2O + Cl involves two heavy atoms, and to the knowledge of the authors, quantum mechanical studies of this reaction without any degree of freedom frozen are extremely hard, if not impossible, at current.

Possible initial orientations of the diatoms are represented in Fig. 4. The z axis was kept parallel to the relative velocity vector. The x axis was an arbitrarily chosen fixed axis of the laboratory system perpendicular to z, and the y axis was such that (x, y, z) forms a cartesian frame. OH was in the (x, z) plane, while HCl was aligned in any direction. The **HO** vector and the z axis formed angle α that we called attack angle, following the usual denomination. b was the impact parameter. Both reagent diatoms were in their rovibrational ground state, and

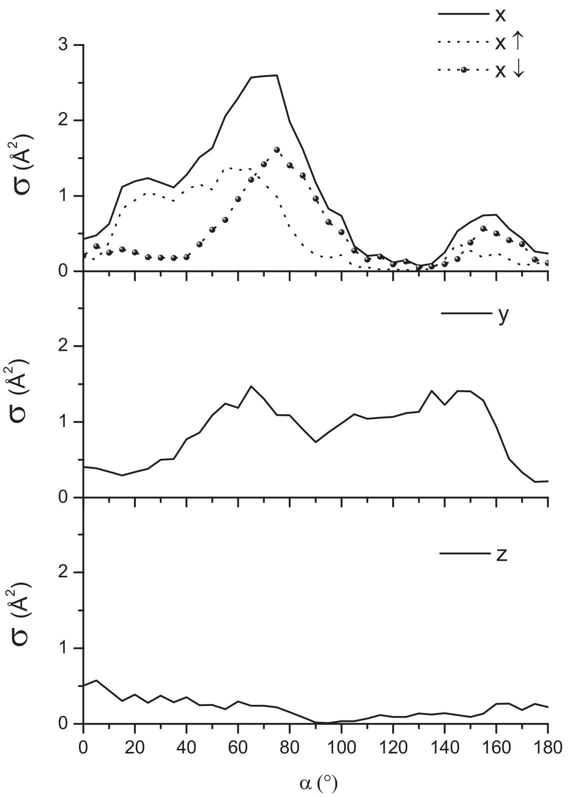

Fig. 5. Reaction cross sections in terms of the attack angle α for the alignment of HCl along the x-axis (upper pannel), y-axis (middle pannel), and z-axis (lower pannel), respectively. The up and down contributions are also shown in the x case.

the collision energy was taken at 7.7 kcal mol^{-1} (a third of eV), a plausible value in a crossed beam experiment. Since the barrier top was at 1.8 kcal mol^{-1}, tunneling was expected to be negligible. The maximum value of b was held at 2.7 Å beyond which no reactive collisions were found.

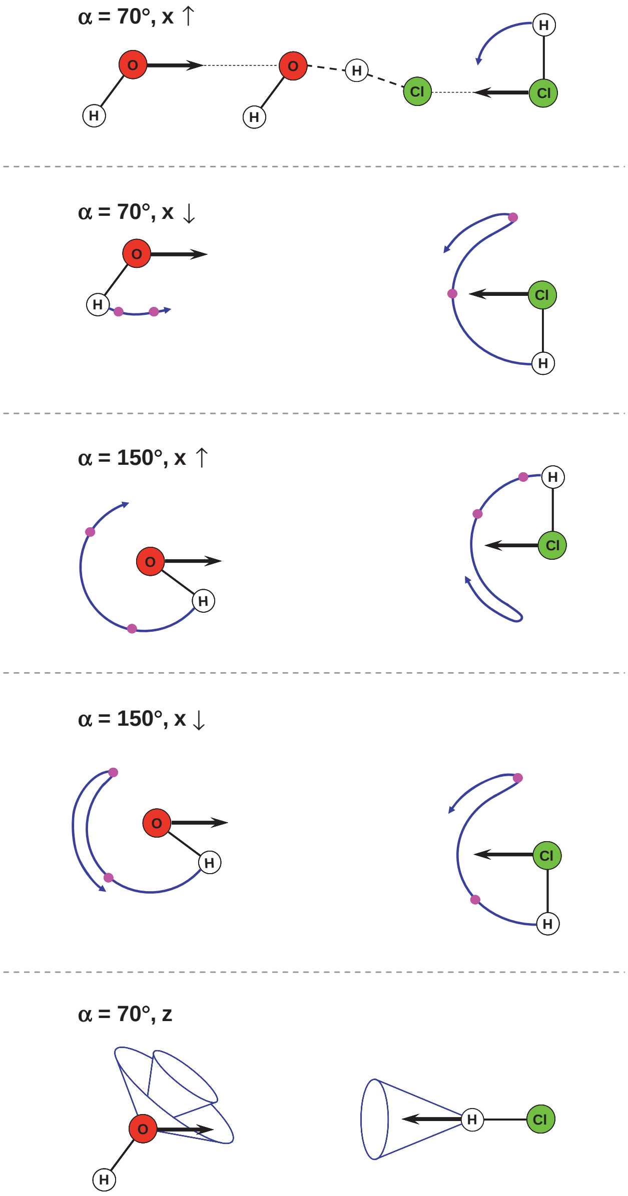

Fig. 6. Typical approach motions of the diatomic molecules en route to the barrier top in terms of their initial orientations. The O and Cl atoms have an almost linear motion up to the barrier top, due to their much larger weight than the H atoms. Circular curves represent H atom pendular motions with respect to the O and Cl atoms. The system at the barrier top is represented for the first trajectory only. Points along the circular curves correspond to given instants and the arrow corresponds to barrier crossing. For the fifth trajectory, O lies in the cone of acceptance carried by HCl while HCl lies simultaneously in the one carried by OH. No reorientation is therefore necessary for the reaction to take place. This kind of approach, however, has only a small contribution to the reactivity (see Fig. 5).

Results and Discussion

The reaction cross sections corresponding to HCl aligned with x, y, and z, are represented in terms of α in Fig. 5 (solid curves labeled x, y, and z). 36 values of α regularly distributed in the range $[0, \pi]$ were considered, and for each value, 4000 trajectories were ran. The contributions due to the two possible orientations of HCl along the x axis (up and down) are also displayed (dashed and dashed-dotted lines labeled $x \uparrow$ and $x \downarrow$). In the y case, the two analogous contributions were both equal to half the total reaction cross section for obvious symmetry reasons. In the z case, no reaction was found when OH comes towards the Cl end of HCl. The x and y curves both had two (main) maxima corresponding to $\alpha \approx 70$ and 150°, respectively. Four typical trajectories associated with these maxima are represented in Fig. 6. A fifth one is also represented which corresponds to the z curve and $\alpha = 70°$. As a matter of fact, strong reorientations involving pendular-like motions took place before barrier crossing, except for the fifth trajectory. In this last case, O was in the cone of acceptance carried by HCl, while HCl was simultaneously in the one carried by OH. The reason is as follows: the shapes of the cones of acceptance are determined by the topology of the PES in the van der Waals well and at the barrier top. At the bottom of the well, the OHCl angle was equal to 175° while at the saddle point (see Fig. 2), it was equal to 144°. On the way to the barrier top, Cl, H, and O were thus roughly aligned. O was thus in

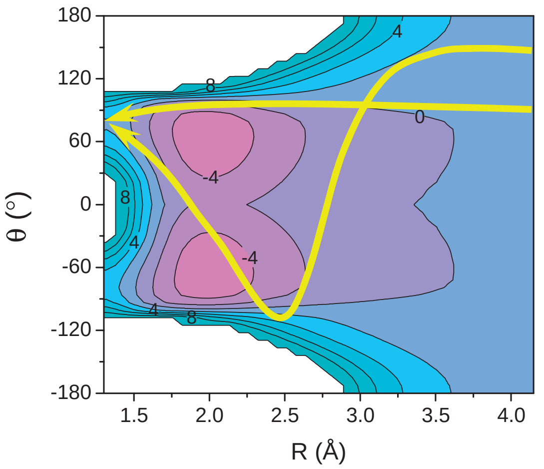

Fig. 7. Relaxed PES in terms of (a) the distance between O and the H atom initially bounded to Cl, and (b) the angle θ between the two OH bonds. The fourth and fifth trajectories in Fig. 6 are schematically represented by the curved and linear paths respectively.

the cone of acceptance carried by HCl. In addition to that, the HOH angle was equal to 114° at the bottom of the well and 102° at the saddle point (see Fig. 2). HCl was thus in the cone carried by OH (the volume lying between two cones is also a conical volume in mathematics). The pathway followed by the system is thus of the same nature as for $Rb + CH_3I$, i.e., linear, and we would expect the reactivity to be very high in such a case. However, comparison between the x, y, and z solid curves in Fig. 5 showed the contrary: at $\alpha \approx 70°$, the reactivity was indeed much higher in the x and y cases than in the z case.

Another surprising finding was the bimodal shape of the x and y curves, especially marked in the x case. The peak around $\alpha = 70°$ was not that surprizing for the reason evoked previously; when the reagents approached each other, HCl was in the cone of acceptance of OH. From this, only the reorientation of HCl necessary for climbing the barrier remained. On the other hand, the peak around $\alpha = 150°$ was unexpected because no fragment lied in the cone of acceptance of the other one. However, the van der Waals well so strongly perturbs the rectilinear motion, on which the ADLOC model is based, that an instinctive grasp of the approach motion of the reagents becomes very hard. In order to shed some light on the reaction mechanism, we have represented in Fig. 7 the relaxed PES in terms of (a) the distance between O and the H atom initially bounded to Cl, and (b) the angle θ between the two OH bonds. Two plausible trajectories are represented. The linear one corresponds to the fifth trajectory in Fig. 6, while the curved one corresponds to the fourth one. The first path is linear, since it roughly follows the reaction path. The second path is associated with the pendular motion of OH because of the strong repulsions from the external wall around θ equal π and minus π at the entrance of the van der Waals well.

Conclusion

We showed by using the quasi-classical trajectory method that for gas-phase chemical reactions like $OH + HCl \rightarrow H_2O + Cl$, which involves a relatively deep pre-barrier van der Waals well, unexpected reaction pathways may be clearly evidenced by controling the spatial orientation of both reagent molecules. The most important pathways were quite complex and far away from the reaction path so that the venerable notion of cone of acceptance did not suffice, on its own, to rationalize steric effects. More work is of course necessary to understand why complex pathways play such an important role in the reactivity of processes involving pre-barrier van der Waals wells.

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