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Trajectory Studies of S_N2 Nucleophilic Substitution. 8. Central Barrier Dynamics for Gas Phase Cl[−] + CH₃Cl

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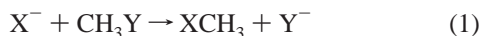
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Received November 27, 2000

Abstract: Quasiclassical direct dynamics trajectories, calculated at the MP2/6-31G* level of theory, are used to study the central barrier dynamics for the Cl[−] + CH₃Cl S_N2 reaction. Extensive recrossings of the central barrier are observed in the trajectories. The dynamics of the Cl[−]–CH₃Cl complex is non-RRKM and transition state theory (TST) is predicted to be an inaccurate model for calculating the Cl[−] + CH₃Cl S_N2 rate constant. Direct dynamics trajectories also show that Cl[−] + CH₃Cl trajectories, which collide backside along the S_N2 reaction path, do not form the Cl[−]–CH₃Cl complex. This arises from weak coupling between the Cl[−]–CH₃Cl intermolecular and CH₃Cl intramolecular modes. The trajectory results are very similar to those of a previous trajectory study, based on a HF/6-31G* analytic potential energy function, which gives a less accurate representation of the central barrier region of the Cl[−] + CH₃Cl reaction than does the MP2/6-31G* level of theory used here. Experiments are suggested for investigating the non-RRKM and non-TST dynamics predicted by the trajectories.

I. Introduction

Bimolecular nucleophilic substitution (S_N2) reactions of the type



are of central importance in gas-phase ion chemistry^{1–3} and organic reaction mechanisms.⁴ In a classic set of experiments, Brauman and co-workers^{5–7} demonstrated that the kinetics of these reactions could be explained by a Walden-inversion mechanism with a double-well potential arising from X[−]–CH₃Y and XCH₃–Y[−] ion–dipole complexes and a [X–CH₃–Y][−] central barrier, in agreement with suggestions from earlier work.^{8,9} Subsequently, this potential model was confirmed by numerous theoretical and experimental studies,^{1,4} including a structural characterization of a S_N2 ion–dipole complex.¹⁰

Given the prominence of statistical theories in chemical reaction dynamics and kinetics,¹¹ it was natural to use these

theories in modeling studies of S_N2 reaction rates.^{1–4} However, more recent detailed examinations of S_N2 reactions of the type in (1) have discovered a range of important nonstatistical attributes,^{12–35} arising from weak couplings between the

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$X-CH_3Y$ intermolecular modes and CH_3Y intramolecular modes. A particularly important feature of this work has been a close relationship between computational,^{12–26} experimental,^{27–36} and theoretical studies.^{35–39} Non-RRKM dynamics for the ion–dipole complexes and a direct substitution reaction pathway driven by C–Y stretch excitation was predicted by collinear quantum dynamical¹² and full-dimensional trajectory calculations.^{2,13–19} These theoretical and computational studies are supported by experimental measurements of the $ClCH_3 + Br^-$ product translational energy following Cl^-CH_3Br dissociation,²⁸ the dependence of the $Cl^- + CH_3Br \rightarrow ClCH_3 + Br^-$ rate constant on reagent translation and CH_3Br vibrational energies,^{29,31} the lifetime of the Cl^-CH_3Cl complex,³² and the mode specific decomposition of the Cl^-CH_3Br complex.³³ These studies have motivated higher dimensional and more accurate quantum dynamical calculations^{24–26} for the $Cl^- + CH_3Cl$ and $Cl^- + CH_3Br$ systems. It is found that their S_N2 reactions are dominated by resonances which have lifetimes that strongly depend on whether the intermolecular or intramolecular modes of the pre-reaction $X-CH_3Y$ complex are excited.²⁶ Nonstatistical dynamics are also seen in experimental³⁴ and trajectory^{20,21} studies of the translational activation of the $Cl^- + CH_3Cl$ S_N2 reaction. The threshold for this process is substantially higher than the actual potential energy barrier and the trajectories show the reaction is direct, without trapping in the ion–dipole complexes. A similar direct reaction is also found for the highly exothermic $F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$ reaction.²²

A potentially very significant finding from the trajectory studies is the trapping of trajectories in the central barrier region of the potential energy surface, with concomitant recrossing of the barrier.^{14,15} The former suggests that vibrational states prepared in the central barrier region may be sufficiently long-lived to resolve their spectra,⁴⁰ while the latter indicates that crossing the central barrier may not be a rate-controlling step, as assumed by statistical theories for many S_N2 reactions.²² To illustrate, the $Cl^- + CH_3Cl$ S_N2 reaction has a central barrier with an energy higher than that of the reactants.⁴¹ Transition state theory (TST) assumes crossing this barrier is rate controlling and the rate constant may be determined from the barrier's free energy.¹⁴ However, if barrier recrossing is significant, TST is an invalid model for interpreting the $Cl^- + CH_3Cl$ rate constant.⁴²

These previous trajectory studies utilized analytic potential energy functions fit to experimental data and HF/6-31G* calculations.⁴³ Though this level of theory correctly represents

many properties of S_N2 potential energy surfaces,⁴⁴ it gives X–C and Y–C bond lengths at the central barrier which are ~ 0.05 – 0.1 Å too long.^{44,45} This difference has been discussed in the literature^{26,41,45} and it has been suggested that a HF analytic potential energy function may give dynamics different from those obtained from a potential energy function calculated from higher and more accurate levels of electronic structure theory.⁴⁵ Scaling the HF/6-31G* potential energy function for $Cl^- + CH_3Cl$, to give a more accurate central barrier structure, is found to affect the reaction probability in reduced dimensionality quantum scattering calculations.²⁵ Since the central barrier dynamics of S_N2 reactions may depend on details of the potential energy surface, it is appropriate to reinvestigate the central barrier dynamics for $Cl^- + CH_3Cl$ at a higher level of theory. However, with recent advances in computer technology and computational algorithms, it is now practical to obtain the gradient for integrating the trajectory directly from an electronic structure theory, without the need for fitting an analytic potential energy function.⁴⁶ In this manner, the exact classical dynamics for a particular electronic structure theory may be determined. This is the approach used here to simulate the $Cl^- + CH_3Cl$ central barrier dynamics at the MP2/6-31G* level of theory. This theory gives a structure and vibrational frequencies for the $[Cl-CH_3-Cl]^-$ central barrier²¹ in excellent agreement with the values for the much higher CCSD(T) theory;⁴¹ i.e., the Cl–C bond lengths of the two theories agree to within 0.005 Å and the symmetric Cl–C and C–H stretches differ by only 6 and 65 cm^{-1} , respectively. The MP2 classical potential energy barrier, without zero-point energy, is 4.54 kcal/mol with respect to reactants. The CCSD(T) value for this barrier is 3.16 kcal/mol and the HF/6-31G* value, used to derive the analytic potential energy function for the earlier study, is 3.57 kcal/mol.

II. Computational Procedure

This direct dynamics trajectory study was performed with the VENUS96/GAUSSIAN98 package of programs,^{21,47–49} which includes an efficient predictor-corrector integration algorithm⁵⁰ and Hessian updating.⁵¹ The numerical integration involves constructing a local quadratic Hamiltonian that is integrated analytically within a specified trust radius.⁴⁶ The resulting coordinates and momenta at the end of

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this step are modified by a corrector algorithm.⁵⁰ Energy conservation at the end of the integrations varied from 0.01 to 0.6 kcal/mol, out of a total energy on the order of 25–31 kcal/mol. A total of 10 trajectories were calculated by sampling 300 K Boltzmann energy distributions at the central barrier for the reaction coordinate, the eleven orthogonal normal modes of vibration, and the three external rotation degrees of freedom. Quasiclassical sampling,⁵² which includes zero-point energy, was used for the vibrations. Each of these trajectories was integrated for 3 ps in both the forward and backward directions off the barrier. As discussed below, the total number of barrier excitation trajectories and integration time considered are sufficient to determine whether RRKM and transition state theory (TST) are accurate for the $\text{Cl}^- + \text{CH}_3\text{Cl}$ S_N2 reaction.

Three trajectories were calculated to study the efficiency of $\text{Cl}^- + \text{CH}_3\text{Cl} \rightarrow \text{Cl}^- - \text{CH}_3\text{Cl}$ association. For these trajectories, the initial impact parameter and center of mass separation are 2 and 16 Å, respectively. As above, 300 K Boltzmann energy distributions were sampled for CH_3Cl , using quasiclassical sampling for the vibrations and treating the rotations classically. Initial conditions were selected that had a $\text{Cl}^- - \text{C} - \text{Cl}$ angle of approximately 180° . The initial $\text{Cl}^- + \text{CH}_3\text{Cl}$ relative translational energy is 1.58 kcal/mol, to represent a 1.00 kcal/mol relative translational energy at infinite separation and an additional 0.58 kcal/mol arising from the $\text{Cl}^- + \text{CH}_3\text{Cl}$ attractive potential at a separation of 16 Å. It requires 92 h on two processors of a Pentium III/733 MHz workstation to integrate a trajectory for 3 ps.

III. Results and Discussion

Before presenting the trajectory results it is useful to review the predictions of RRKM theory and TST for the trajectory dynamics.

Previous anharmonic RRKM calculations predict that, for the energy corresponding to a 300 K Boltzmann distribution at the central barrier, the average lifetime of the $\text{Cl}^- - \text{CH}_3\text{Cl}$ complex is 4 ps. Thus, RRKM theory predicts that 50%, i.e., $\exp(-3/4)$, of the $\text{Cl}^- - \text{CH}_3\text{Cl}$ complexes formed by movement off the central barrier should form $\text{Cl}^- + \text{CH}_3\text{Cl}$ products. In addition, because of the higher potential energy at the central barrier in comparison to that for the products and the much tighter transition state at the central barrier compared to that for dissociation, RRKM theory predicts that $\text{Cl}^- - \text{CH}_3\text{Cl}$ preferentially dissociates to $\text{Cl}^- + \text{CH}_3\text{Cl}$ with negligible recrossing of the central barrier. Thus, crossing the central barrier is the rate-controlling step of the S_N2 reaction, as assumed by TST.¹¹ It should be noted that, according to RRKM theory, the MP2 level of theory used here should give less central barrier recrossing compared to the presumably much more accurate CCSD(T) level of theory, which has a lower central barrier.

A. Barrier Excitation Trajectories. A most striking feature of the trajectories initiated at the central barrier is that their dynamics are significantly different from that assumed by RRKM theory, and instead, quite similar to what was found in the previous trajectory study.¹⁴ Not one of the twenty 3 ps backward and forward integrations off the central barrier formed $\text{Cl}^- + \text{CH}_3\text{Cl}$ products, while as discussed above, RRKM theory predicts 50%, i.e., ten, of these integrations should have formed products. Many of the trajectories exhibit a regular type motion, with well-identified frequencies for the $\text{Cl}-\text{C}$ stretching motions and extensive recrossing of the central barrier. This is illustrated in Figure 1, where the two $\text{C}-\text{Cl}$ bond lengths, R_1 and R_2 , are plotted versus time for three of the trajectories.

Of the 10 trajectories calculated here, the trajectory with the most regular motion is shown in the top graph in Figure 1. There are two crossings of the central barrier for the trajectory and,

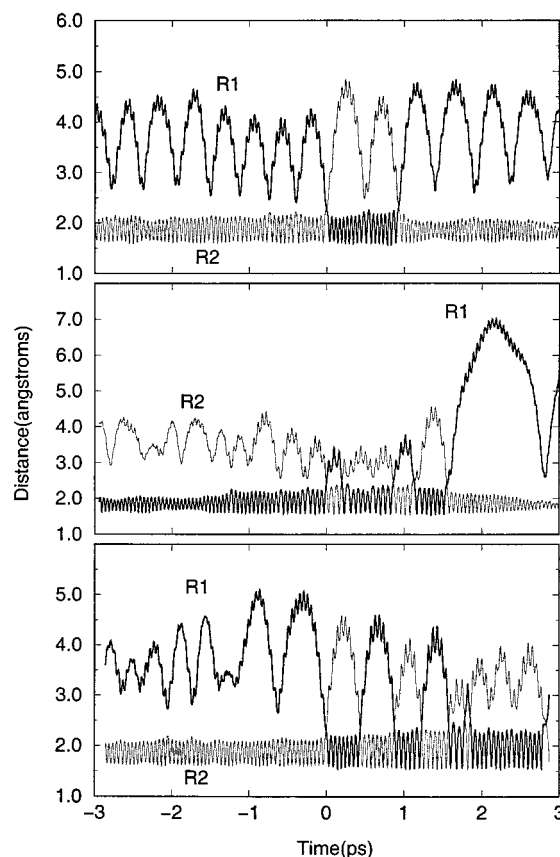


Figure 1. Representative trajectories for excitation at the $[\text{Cl}-\text{CH}_3-\text{Cl}]^-$ central barrier. The trajectories are initiated at time equal zero and integrated for 3 ps in both the forward and backward directions. The dark line is R_1 and the light line R_2 .

after 3 ps of motion in both the forward and backward directions off the central barrier, the trajectory starts and ends in the same $\text{Cl}^- - \text{CH}_3\text{Cl}$ complex. The middle trajectory in Figure 1 has the most irregular motion of the trajectories integrated. The bottom trajectory has the most central barrier recrossings, i.e., eight.

Transition state theory assumes that each crossing of the central barrier leads to reaction.¹¹ A total of 29 central barrier crossings occurred for the 10 trajectories. However, since no S_N2 reactions occurred, it is not possible to determine a definitive correction to TST. An estimate of this correction may be made by assuming each trajectory that started in one $\text{Cl}^- - \text{CH}_3\text{Cl}$ complex and ended in the other will ultimately be a reaction event. Five trajectories are of this type and dividing this number by 29, the number of barrier crossings, gives a TST correction factor of 0.2, which is similar to the 0.1 correction factor estimated from the previous trajectory study¹⁴ based on an analytic potential energy function. This latter value is an upper limit¹⁴ as is the former value, since none of the trajectories evaluated here reached the $\text{Cl}^- - \text{CH}_3\text{Cl}$ asymptote and more recrossings of the central barrier are expected before this asymptote is reached for both the backward and forward integrations of the trajectories.

Figure 1 shows there is a large difference between the vibrational frequencies of the $\text{Cl}^- - \text{C}$ ion-dipole and $\text{Cl}-\text{C}$ covalent bonds, and that the $\text{Cl}^- - \text{C}$ frequency is modulated by the $\text{Cl}-\text{C}$ frequency. The coupling between the $\text{Cl}^- - \text{C}$ bond and $\text{Cl}-\text{C}$ bonds increases as the $\text{Cl}^- - \text{C}$ bond shortens, which causes the $\text{Cl}-\text{C}$ frequency to decrease when the $\text{Cl}^- - \text{C}$ bond is in the vicinity of its inner turning point. In the top graph of Figure 1, the $\text{Cl}^- - \text{C}$ frequency varies from ~ 70 – 85 cm^{-1} and

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the average Cl–C frequency is 630–650 cm^{-1} . The latter frequency becomes as low as $\sim 480\text{--}550\text{ cm}^{-1}$ at the Cl–C inner turning point. If all 10 trajectories are considered, the average Cl–C frequency varies from 590 to 710 cm^{-1} , while the variation in the Cl–C frequency is much greater, ranging from 35 to 170 cm^{-1} .

B. $\text{Cl}^- + \text{CH}_3\text{Cl}$ Collision Trajectories. Not one of the three trajectories, calculated to simulate $\text{Cl}^- + \text{CH}_3\text{Cl}$ collisions, formed a $\text{Cl}^- - \text{CH}_3\text{Cl}$ complex. For each, Cl^- “bounced off” CH_3Cl with only one inner turning point in the $\text{Cl}^- + \text{CH}_3\text{Cl}$ center of mass motion. The initial Cl–C–Cl angle is $\sim 180^\circ$ for each of these trajectories, with Cl^- colliding backside along the $\text{S}_{\text{N}}2$ reaction path. The absence of complex formation in these trajectories is consistent with the previous extensive trajectory study utilizing an analytic potential energy surface,¹³ which showed that $\text{Cl}^- + \text{CH}_3\text{Cl} \rightarrow \text{Cl}^- - \text{CH}_3\text{Cl}$ does not occur by translation-to-vibration ($\text{T} \rightarrow \text{V}$) but translation-to-rotation ($\text{T} \rightarrow \text{R}$) energy transfer. For oriented collisions, i.e., a Cl–C–Cl angle of $\sim 180^\circ$, and collisions with small impact parameters such as the 2 Å value used here, $\text{T} \rightarrow \text{R}$ energy transfer is negligible and $\text{T} \rightarrow \text{V}$ is required for complex formation. The inefficient $\text{T} \rightarrow \text{V}$ energy transfer arises from weak coupling between the $\text{Cl}^- - \text{CH}_3\text{Cl}$ intermolecular and CH_3Cl intramolecular modes. A similar weak coupling occurs in the barrier excitation trajectories, where extensive recrossing of the central barrier is observed instead of dissociation to $\text{Cl}^- + \text{CH}_3\text{Cl}$ as predicted by RRKM theory.

IV. Summary

An important finding from this study is that MP2/6-31G* direct dynamics gives similar non-RRKM and non-TST dynamics for the $\text{Cl}^- + \text{CH}_3\text{Cl}$ $\text{S}_{\text{N}}2$ reaction as found in a previous trajectory study¹³ based on an analytic potential energy function. This is an important result, since the MP2/6-31G* level of theory gives a more accurate representation of the central barrier region of the potential energy surface than does the analytic potential energy function, which was developed from experimental data and HF/6-31G* calculations. Future studies of the $\text{Cl}^- + \text{CH}_3\text{Cl}$ $\text{S}_{\text{N}}2$ reaction may take several directions. An important advance would be to identify the classical phase space structure and coordinate system that links the weak coupling between the $\text{Cl}^- - \text{CH}_3\text{Cl}$ intermolecular and CH_3Cl intramolecular modes, resulting in non-RRKM dynamics for the $\text{Cl}^- - \text{CH}_3\text{Cl}$ complex, with the weak coupling giving rise to the central barrier recrossings. Comparisons of classical and quantum dynamics, performed on highly accurate reduced-dimensional potential energy surfaces,⁴¹ would be very beneficial for this analysis. That the $\text{Cl}^- + \text{CH}_3\text{Cl}$ reaction dynamics is nonstatistical for the full-dimensional system, as shown by the direct dynamics trajectories reported here, gives credence to studying the nonstatistical dynamics of reduced dimensionality models. Such studies may lead to a theory explaining why the $\text{Cl}^- + \text{CH}_3\text{Cl}$ reaction dynamics is nonstatistical, while the related $\text{Cl}^- + \text{ClCH}_2\text{CN}$ reaction has statistical dynamics.⁵³

It should be noted that one of the limitations of classical trajectory simulations is that they do not constrain zero-point energy motions and, thus, allow a vibrational mode's energy to fall below the zero-point level during the course of the trajectory.^{54–56} Although the internal modes are constrained to have at least zero-point energy in the initial conditions, this constraint is not imposed during the classical trajectory. Transfer of energy between the vibrational modes and the reaction coordinate could lead to enhanced recrossing that would not be seen in a more accurate quantum mechanical study. However, since quantum dynamics is often more regular than classical dynamics,^{56,57} it is also possible that quantum dynamics may have more recrossings. Comparisons of classical and quantum central barrier dynamics for $\text{Cl}^- + \text{CH}_3\text{Cl}$ reduced dimensionality models, for which quantum dynamics are feasible, would be of particular interest.

Experimental investigations of the non-RRKM and non-TST dynamics, predicted for the $\text{Cl}^- + \text{CH}_3\text{Cl}$ system by the MP2/6-31G* direct dynamics simulations, are important. A significant amount of barrier recrossing will make the experimental $\text{S}_{\text{N}}2$ thermal rate constant smaller than that predicted by a TST calculation based on an accurate central barrier energy and structure. Additional experimental measurements of this rate constant,⁴² including its temperature dependence, would be very helpful. Barrier recrossing dynamics could also be probed by investigating the central barrier region with femtochemistry⁵⁸ and/or a time-independent spectroscopic technique.⁵⁹ If a wave packet remains localized in the central barrier region, it may then be possible to resolve its vibrational dynamics and spectrum. A direct probe of non-RRKM dynamics for the $\text{Cl}^- - \text{CH}_3\text{Cl}$ complex would involve measuring the lifetime of its resonance states. Both classical^{13,14,16} and quantum²⁶ dynamics calculations indicate that they are highly mode specific, giving rise to the intrinsic non-RRKM⁶⁰ dynamics for the $\text{Cl}^- - \text{CH}_3\text{Cl}$ complex.

Acknowledgment. This research was supported by the National Science Foundation. The authors wish to thank the Schlegel research group for their help in developing and maintaining the VENUS/GAUSSIAN computer program package.

JA004077Z

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