Photoactivation of the Cl⁻ + CH₃Br S_N2 Reaction via Rotationally Resolved C−H Stretch Excitation of the Cl⁻·CH₃Br Entrance Channel Complex

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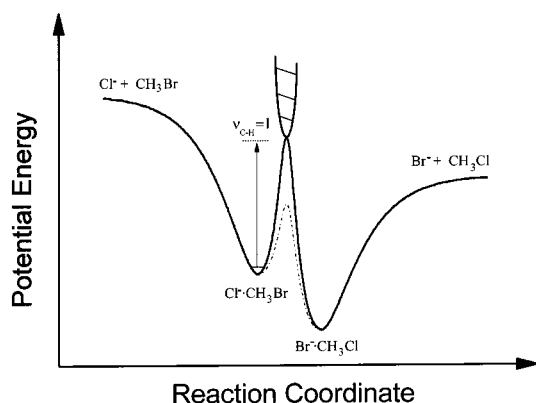P.O. Box 208107, New Haven, Connecticut 06520-8107*

The gas-phase S_N2 reaction,[1]

$$X^- + CH_3Y \rightarrow Y^- + CH_3X \tag{1}$$

involving halide (X,Y) exchange, is the archetypal ion−molecule reaction taking place over a double minimum potential energy surface.[2] These minima correspond to ion−dipole complexes, and are separated by the Walden inversion barrier as depicted in Figure 1. Surprisingly, despite the fact that this double minimum surface is ubiquitous in ion chemistry,[1−3] these minima have not yet been characterized spectroscopically,[4] nor do we have any direct determinations of the transition state energy relative to the reactant minimum.[5] In this paper, we report an infrared spectroscopic study of the Cl⁻·CH₃Br and Br⁻·CH₃Cl entrance and exit channel complexes of the exothermic reaction:

$$Cl^- + CH_3Br \rightarrow Br^- + CH_3Cl \tag{2}$$
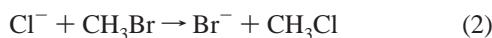
to directly challenge the predicted Cl⁻·CH₃Br structure.[6] Moreover, a glance at Figure 1 indicates that for this (and other) exothermic S_N2 reaction, the transition state lies below the energy of reactants,[8,9] so that excitation of the high-frequency (C−H stretch) vibrations can trigger reaction, but not dissociation of the Cl⁻·CH₃Br entrance channel complex. This strategy affords the opportunity to determine the efficacy of intramolecular vibrations in promoting the reaction, and enables a detailed characterization of the nonstatistical kinetics displayed by both
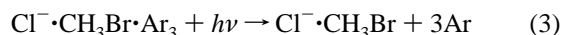
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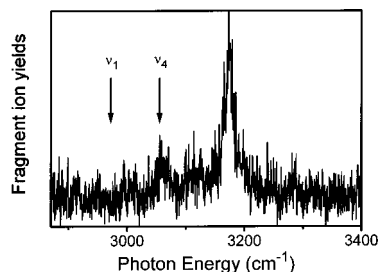(12) Cyr, D. M.; Bishea, G. A.; Han, C.-C.; Posey, L. A.; Johnson, M. A. *SPIE Proc.* **1992,** *1638,* 74−84.
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Figure 1. Schematic potential energy curve describing the reaction coordinate in the Cl⁻ + CH₃Br → Br⁻ + CH₃Cl reaction. The height of the transition state is presently in question. The ab initio value[21,22] is presented with the solid line, while the lower value extracted from thermal decomposition[5] of Cl⁻·CH₃Br is shown by the dotted line.

the bimolecular reaction[7] and the metastable decomposition of the hot entrance channel complex.[8,9] The Cl⁻·CH₃Br and Br⁻·CH₃Cl (entrance and exit channel) complexes were prepared independently by electron impact ionization/secondary electron attachment[10] to appropriate neutral precursors in a supersonic free jet, as described in previous publications.[11,12] In the earlier work, threshold photodetachment and collision-induced dissociation (CID) were used to verify the integrity of their syntheses. The Cl⁻·CH₃Br species formed here (made with CCl₄/CH₃Br) displayed the 1:1 Cl⁻/Br⁻ high collision energy CID pattern characteristic of the entrance channel,[11,12] while the putative Br⁻·CH₃Cl complex (made with CH₂Br₂/CH₃Cl) dissociated exclusively into Br⁻ upon CID.

In our spectroscopic studies of other strongly bound ion−molecule complexes (such as X⁻·H₂O),[13] we have found it nontrivial to quench them into their minimum energy structures by bimolecular collisions in the jet.[14] However, we have routinely generated cold clusters using an argon cluster-mediated synthesis technique,[15] and we applied this method to generate both S_N2 complexes. For example, to generate the entrance channel complex, the method relies on ligand switching between CH₃Br and argon atoms in Cl⁻·Ar_n precursor clusters.

After preparation, the complexes drift about 15 cm in the free jet prior to injection into a tandem time-of-flight photofragmentation mass spectrometer,[10] where they are excited by the output from a pulsed infrared laser (Laser Vision optical parametric oscillator). To excite the weak C−H stretching transitions, the IR laser beam (1 mJ/pulse, bandwidth 2 cm⁻¹) is passed many times through the ion packet using a multipass cell.[16] Product ions are mass analyzed by using a reflectron configuration. Spectra are acquired in an action mode by monitoring the photoinduced fragment ion intensity with a boxcar integrator while the laser is scanned through the range of the C−H stretching chromophore (2870−3400 cm⁻¹), and result from summing 15−20 individual scans.

To identify the spectral signature of the entrance channel complex cooled to the minimum energy structure, we first acquired the spectrum of the argon-solvated complex (which is readily generated under these cold source conditions) via argon predissociation spectroscopy:[15]

$$Cl^- \cdot CH_3Br \cdot Ar_3 + h\nu \rightarrow Cl^- \cdot CH_3Br + 3Ar \tag{3}$$

The argon predissociation spectrum from Cl⁻·CH₃Br·Ar₃ is displayed in Figure 2, revealing two significant features at 3063

Figure 2. IR (Ar) predissociation spectra of $Cl^-\cdot CH_3Br\cdot Ar_3$ (obtained by detection of $Cl^-\cdot CH_3Br$ photoproducts). Arrows show ν_1 and ν_4 (symmetric and asymmetric) stretching modes of bare CH_3Br.[17]

Figure 3. Infrared predissociation spectra of (a) $Cl^-\cdot CH_3Br$ (obtained by detection of Br^- reaction products) and (b) $Br^-\cdot CH_3Cl$ (also obtained by detection of Br^-). The arrow shows the location of the entrance channel complex band origin obtained in the argon predissociation spectrum (Figure 2). Labels indicate the (lower K) assignment of the structure to Q-branches of a perpendicular transition.

and 3175 cm^{-1}. These bands are blue-shifted relative to the bare CH_3Br transitions (labeled ν_1 and ν_4, occurring at 2972 and 3056 cm^{-1}),[17] with an increased splitting between the bands (84 vs 112 cm^{-1} for bare and complexed CH_3Br, respectively). This blue shift and opening of the splitting was anticipated by Hase's potential surface,[18] which predicts (anharmonicity corrected) bands at 3055 and 3163 cm^{-1} in the C_{3v} complex, quite close to the experimental values. Note that we have recovered these calculated values using anharmonicity corrected frequencies from Gaussian 94 [B3LYP/6-31G(d)],[19] and extended these calculations to the higher energy C_{3v} isomer arising from the "frontside" attachment of Cl^- to bromine.[20] The frontside isomer is predicted to display infrared transitions to the red of those arising from bare CH_3Br (at 2932 and 3003 cm^{-1}, respectively), while the backside (methyl pocket) isomer yields blue-shifted bands in agreement with those found experimentally.

Having identified the band origins from the cold, argon-solvated complex, we then scanned the spectrum of bare $Cl^-\cdot CH_3Br$. The resulting spectrum of the 3175 cm^{-1} band is displayed in Figure 3, where the origin from the argon complex (arrow) evolves into a resolved set of evenly spaced peaks. The 3063 cm^{-1} band, while also broadened, does not yield well-resolved structure.

Excitation of both (3063 and 3175 cm^{-1}) features in $Cl^-\cdot CH_3Br$ primarily results in production of Br^- ions, with a small amount of Cl^- (<10% of the Br^- yield). However, the photoinduced Cl^- yield was nearly constant over the 3100−3300 cm^{-1} scan, such that the sharp spectrum (Figure 3) was not evident when monitoring Cl^-. Off resonant, both Br^- and Cl^- are produced, an effect that we attribute to excitation of hot complexes, since only these have sufficient energy (after ~3100 cm^{-1} excitation) to reach the reactant asymptote [$\Delta H^\circ(Cl^-\cdot CH_3Br) = 4370$ cm^{-1}].[21]

We also scanned the spectrum from the exit channel complex with the result shown in Figure 3b. Like the hot entrance channel species detected via the Cl^- product channel, this complex displays very broad, unresolved bands throughout the 3000−3300 cm^{-1} range, except that in this case, no Cl^- was detected. The

lack of a resolved spectrum from the exit channel complex is consistent with the most recent determination[21] of its bond strength ($\Delta H^\circ = 3810$ cm^{-1}), which precludes observation of cold complexes in one-photon spectroscopy.

Because the dissociation channels lie above the energy range of the C−H stretches, the fact that we observe the band *origin* in $Cl^-\cdot CH_3Br$ action spectroscopy requires passage through the lower lying Walden inversion transition state to yield Br^-. The (3175 cm^{-1}) transition energy is very close to the 3000−3200 cm^{-1} range expected from ab initio calculations[22,23] (and kinetic modeling of the bimolecular reaction rates[8,21,24]) providing us with an opportunity to study the transition state region of this reaction at spectroscopic resolution. On the other hand, thermal decomposition of the entrance channel complex[5] occurs with an Arrhenius parameter of only about 1570 ± 200 cm^{-1}, well below the observed transitions. The lower barrier would imply that our sharp spectra appear as much as 1600 cm^{-1} into the continuum. The fact that the observed transitions are sharp would then require inefficient coupling of the C−H modes to the reaction coordinate, consistent with Viggiano's observation[7] (considered theoretically by Hase[18] and Clary[25]) that excitation of the intramolecular modes does not affect the reaction rate.

Finally, we consider the origin of the sharp structure in the 3175 cm^{-1} band of the $Cl^-\cdot CH_3Br$ complex (Figure 3a). The (10 ± 1 cm^{-1}) spacing in the spectrum is very close to twice the A rotational constant of bare CH_3Br (5.08 cm^{-1}),[17] which involves rotation of the hydrogens about the C−Br axis. This behavior is expected for a perpendicular transition of a symmetric top, where Q-branches of the K-stacks are spaced by ~2A. On this basis, we assign the band to the degenerate (E) C−H stretching mode of a C_{3v} symmetry complex. Note that the simplicity of the envelope, with only three strong Q-branches, establishes that our synthesis of the entrance channel complex is achieved with low angular momentum ($K \lesssim 2$), especially when one considers the fact that the nuclear spin statistics effectively freeze the population in $K = 1$.

Summarizing, the band contours and positions definitively establish that this complex adopts C_{3v} symmetry with the chloride ion bound to the hydrogens in the methyl "pocket".

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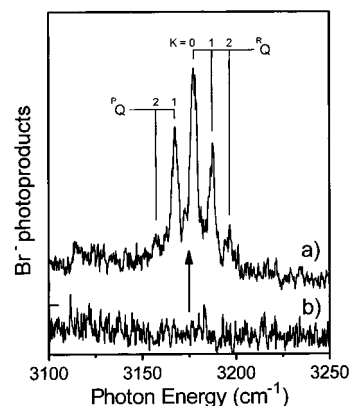(20) Cyr, D. M.; Scarton, M. G.; Wiberg, K. B.; Johnson, M. A.; Nonose, S.; Hirokawa, J.; Tanaka, H.; Kondow, T.; Morris, R. A.; Viggiano, A. A. *J. Am. Chem. Soc.* **1995,** *117,* 1828−1832.
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