a dioxetane intermediate may provide the key to understanding the mechanism of action of vitamin K.

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Temperature Dependence of the Kinetic Isotope Effect for a Gas-Phase S_N2 Reaction: $Cl^- + CH_3Br$

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The study of ion reactions in the gas phase continues to provide a host of new insights into organic reactivity.[1] Kinetic isotope effects (KIEs) are traditionally considered the most sensitive experimental probes of transition-state structure for reactions at well-defined temperatures.[2] Very recently several KIEs have been measured at room temperature for gas-phase S_N2 and E2 reactions.[3] In this paper we report a measurement of the temperature dependence of the deuterium KIE for the reaction $Cl^-(g) + CH_3Br(g) \rightarrow CH_3Cl(g) + Br^-(g)$ and a molecular modeling study to interpret the results.

The experiments were performed in a variable-temperature selected ion flow drift tube (VT-SIFDT). The measurements of the absolute rate constants are standard, and the apparatus is described elsewhere.[4] While the error limit on the absolute rate constants is ±25%, the KIE was measured much more accurately. All conditions (flow rates, pressure, temperature, tuning, etc.) were kept identical when changing isotopes, and the experiments on CH_3Br and CD_3Br were done very close to one another in time. As a result, the errors that contribute to the determination of the KIE are in the determination of the decay of the Cl^- signal with added neutral reactant and in the ratio of the gas correction factors for CH_3Br and CD_3Br used in measuring the reactant gas flow rates. The gas correction factor depends only on the heat capacity of the gas,[5] which can be calculated using the known vibrational frequencies of CH_3Br[6] and CD_3Br.[7] At least five determinations of the decay rate were made for each gas at each temperature. A future paper will report temperature-dependent drift-tube studies of this reaction in order to study the effect of the internal temperature of the CH_3Br and CD_3Br on the reactivity.

Table I. Reaction Rates and Kinetic Isotope Effects for $Cl^-(g) + CH_3Br(g)$

	k_H, cm^3 molecule^{-1} s^{-1}		k_H/k_D	
T, K	expt[a]	theory[b]	expt	theory[b]
207	3.1×10^{-11}	5.3×10^{-11}	0.81 ± 0.03	0.88
300	2.4×10^{-11}	2.4×10^{-11}	0.81 ± 0.03	0.93
538	1.4×10^{-11}	1.6×10^{-11}	0.89 ± 0.06	0.97
564	1.5×10^{-11}	1.6×10^{-11}		0.97

[a] Twenty-five percent uncertainty in absolute value, 15% for relative values. [b] Canonical variational transition state theory and conventional transition-state theory yield the same results to the precision shown in these cases. Also the maximum of the vibrationally adiabatic ground-state potential curve is below the zero-point energy of reactants for both isotopic versions of the reaction so the semiclassical transmission coefficient[10] is unity. There is only one maximum in the free energy of activation profile (at any of these temperatures for either isotope) in the region between the ion–dipole complexes, and the free energy of activation associated with the central barrier is considerably larger than that associated with ion–molecule association; thus there would not be a significant difference if we used the canonical unified statistical theory[10a] instead of canonical variational theory.

The molecular modeling effort is based on direct dynamics calculations[8] employing canonical variational transition state theory (CVT).[9,10] The force field is modeled by neglect of diatomic differential overlap[11,12] with specific reaction parameters (NDDO-SRP)[13] molecular orbital theory. We started with the Austin model 1 (AM1)[12] parameters and the adjustment in the atomic core matrix element U_{pp}^{Cl} made previously[13] for the $Cl^-(g) + CH_3Cl(g)$ reaction. Then we adjusted U_{pp}^{Br} (−76.25 eV) and U_{pp}^{C} (−40.705 eV) to the exoergicity (−6.3 kcal) and room temperature rate constant for the isotopically unsubstituted case. The resulting classical barrier height is −1.5 kcal, i.e., the saddle point is 1.5 kcal below the energy of reactants.

The reaction rates for the unsubstituted reaction are given in Table I. The increase in the experimental rate at 564 K is smaller than the error bars, but it is also observed in the theoretical results, which show minima at 548 and 558 K for CH_3Br and CD_3Br, respectively. Interestingly, the previous study of CH_3Br by

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Caldwell et al.[14] showed a minimum around 530 K although those authors interpreted their data with a linear Arrhenius fit. It would be interesting to carry out experiments at higher *T* to confirm the minimum.

The KIEs are also compared in Table I. The experiments show that the KIE increases by 1.10 ± 0.08[15] over the range studied. Theory also predicts an increasing KIE by approximately the same amount, 10%. Both theory and experiment agree with the previously measured result[3] that the KIE is inverse at 300 K. The theoretical model indicates that the inverse KIE is due to both low-frequency (<300 cm^{-1}) transitional modes (i.e., modes that correlate with zero frequency at reactants) and C–H stretches, whose frequencies are higher at the transition state than at the reactants. Furthermore it indicates that the C–H stretches dominate the *T* dependence of the KIEs. Extended basis set ab initio SCF calculations[16] of reactant and transition-state frequencies confirm the qualitative correctness of these low- and high-frequency effects. Use of the ab initio C–H stretch frequencies both lowers the predicted KIEs and increases their *T* dependence (this may be the dominant error in the semiempirical modeling effort). The present results provide experimental support for previous theoretical work[13,17] on the $Cl^- + CD_3Cl$ and $H + HCD_3$ reactions which implicated both C–H stretches and low-frequency transitional modes as strong contributors to inverse α-deuterium secondary KIEs.

These studies suggest that the measurement and modeling of the temperature dependence of kinetic isotope effects are a sensitive probe of organic transition states for gas-phase reactions.

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Emission of Radiation by Collisionally Activated Ions: A New Approach to Ion Structure Determination

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Experimental techniques for assigning structures to polyatomic organic ions in the gas phase have been vigorously developed over the past 20 years and were reviewed in 1985.[1] The chief methods have involved ion energetics and mass spectral fragmentation behavior. The collision-induced dissociation (CID) of mass-selected, fast (keV) ion beams has provided vital information for ion structure assignment. Many ingenious collision-based methods have been described, e.g. charge stripping,[2] charge reversal,[3] neutralization–reionization,[4] angle resolved mass spectrometry,[5] and surface-induced dissociation,[6] but their limitation lies in that they all produce another mass spectrum which must then be empirically analyzed. With this in mind the present work was begun to investigate the relationship between ion structure, fragmentation characteristics, and the collision-induced emission of radiation.

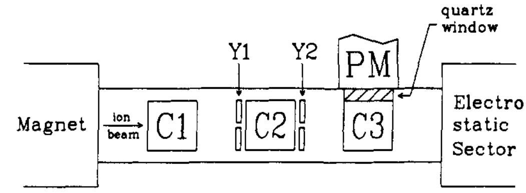

Figure 1. Schematic diagram of the experimental region of the mass spectrometer (details in text).

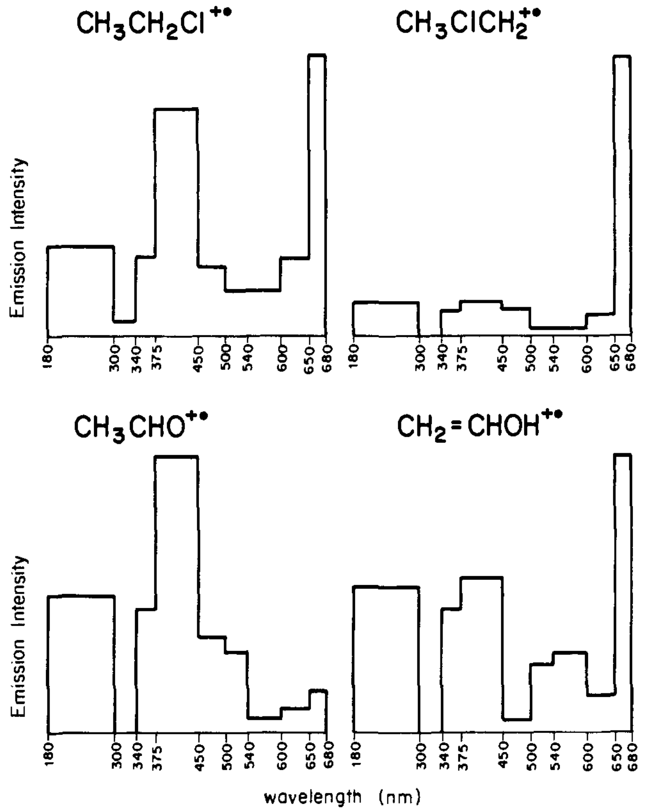

Figure 2. Collision-induced emission spectra for $CH_3CH_2Cl^{\bullet+}$, $CH_3ClCH_2^{\bullet+}$, $CH_3CHO^{\bullet+}$, and $CH_2{=}CHOH^{\bullet+}$. He target gas in collision cell C2; 80% beam transmission; emission intensity in arbitrary units.

To study light emitted by collisionally excited ions, a new collision cell was constructed for the second field-free region of our VG ZAB-2F mass spectrometer[7] (Figure 1). C1 and C2 are conventional collision cells. Y1 and Y2 are variable *y*-axis ion beam collimating slits. The new cell, C3, has a quartz window and highly polished interior. Radiation from ions excited by collision in C1, C2, or C3 is detected by a photomultiplier (THORN EMI 9924QB) placed beyond the quartz window. For the preliminary experiments described here, spectra were obtained by sequentially placing eight wavelength cutoff filters[8] between the window and the photomultiplier, dividing its response range (180–680 nm) into nine regions (see Figure 2). The spectra were corrected for the average photomultiplier response over each region. Without data accumulation, signal-to-noise was between 10 and 2, depending on the wavelength (PM response). Signal averaging (5–10 min) sufficed reliably to measure weak signals,

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