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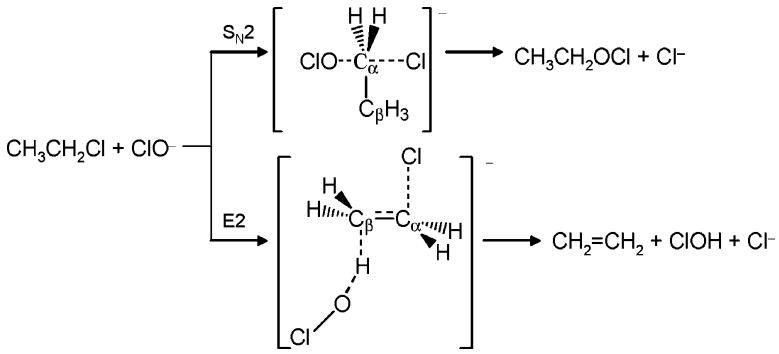

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Deuterium Kinetic Isotope Effects in Gas-Phase S_N2 and E2 Reactions: Comparison of Experiment and Theory

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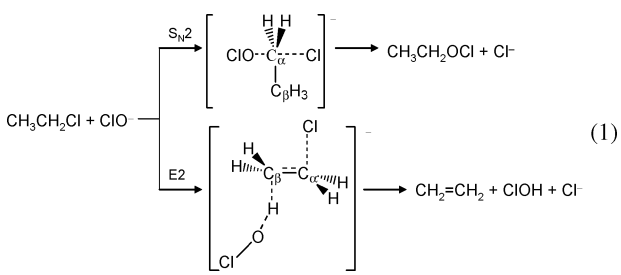
The competition between nucleophilic substitution and base-induced elimination has been well-documented in the condensed phase; however, few studies have addressed this competition in the gas-phase. Studying S_N2 and E2 reactions in the gas-phase allows one to gain insight into intrinsic features that affect this competition without interference from solvent effects. However, these experiments are inherently difficult since these mechanisms generate the same ionic product and detection of neutral products presents serious analytical challenges.

Several groups have investigated S_N2 and E2 reactions theoretically; however due to the lack of experimental data, less work has addressed the competition between these two reactions. Hu and Truhlar[1] have evaluated the reaction rate constants and deuterium kinetic isotope effects (KIE $= k_H/k_D$) for both the S_N2 and E2 pathways of the reaction of ClO^- with C_2H_5Cl, shown in eq 1.



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Their work has provided us with the unique opportunity to compare theory and experiment. In this account we report experimental, overall reaction rate constants and deuterium KIEs for the reactions of $RCl + ClO^-$ (R = methyl, ethyl, isopropyl, and *tert*-butyl). This systematic approach indicates that, for the reaction of ClO^- with C_2H_5Cl, both the S_N2 and E2 channels occur, as predicted by Hu and Truhlar; however the experimental KIE differs drastically from the computational predictions.

There is extensive literature on gas-phase reactions that occur exclusively by S_N2 or by E2 mechanisms. (See refs 2−6 and citations therein.) For reactions that can occur by both pathways, Gronert[7] has provided an excellent summary of experimental approaches,[8−13] including his novel utilization of dianionic nucleophiles that yield diagnostic product ions.[14,15] Our research has utilized reactivity trends[16] as well as kinetic isotope effects[17] to explore these processes.

Kinetic isotope effects can be used to distinguish between S_N2 and E2 mechanisms if the reaction proceeds at a rate slower than the collision rate.[18] For E2 reactions normal KIEs ($k_H/k_D > 1$) are observed, while for S_N2 reactions inverse KIEs ($k_H/k_D < 1$) are observed. The origin of these effects is primarily a result of changes in vibrational frequencies as the reaction proceeds from the reactants to the transition state structure.[19] Deuteration lowers the vibrational frequencies in both the reactants and transition states relative to the undeuterated compounds. An E2 reaction proceeds through a transition state where the C_β−H bond is partially broken thus lowering these frequencies relative to reactants. Since the frequencies for the undeuterated species are lowered more substantially than those for the deuterated species in the transition state, $E_H^\ddagger < E_D^\ddagger$. An S_N2 reaction proceeds through a trigonal planar transition state where the C_α−H bonds are tightened, thus raising these frequencies relative to reactants. Since the frequencies for the undeuterated species are raised more substantially than those for the deuterated species in the transition state, $E_H^\ddagger > E_D^\ddagger$. When both reaction pathways are viable an overall KIE is measured which provides qualitative insight into the competition between these mechanisms.

Hu and Truhlar[1] have quantitatively evaluated the competition between S_N2 and E2 pathways for ClO^- with C_2H_5Cl and with C_2D_5Cl using dual-level generalized transition state theory and statistical calculations based on high-level, correlated electronic structure calculations using extended basis sets (MP2/ADZP).[1] Their calculations predict an S_N2 reaction efficiency of 2% with a deuterium KIE of 0.60 and an E2 reaction efficiency of 26% with a deuterium KIE of 3.1 at 300 K. They predict an overall reaction efficiency of 28% and a KIE of 2.4.

We have measured the overall reaction rate constants and KIE for the reactions of $RCl + ClO^-$ (R = methyl, ethyl, isopropyl, and *tert*-butyl) using a tandem flowing afterglow-selected ion flow tube instrument, FA-SIFT.[20,21] ClO^- is an ideal choice for a nucleophile because the rate constants for the entire neutral series, methyl through *tert*-butyl, are within a measurable window of 10^{-9}−10^{-13} cm^3 molecule^{-1} s^{-1} and are all below the calculated collision rate so that KIEs are evident. The reactant ion was formed in the source flow tube from electron impact on N_2O to produce O^- which was then allowed to react with CCl_4 to form ClO^-. ClO^- ions were mass-selected and injected into the reaction flow tube where they were thermalized to 304(±2) K by collisions with He buffer gas (0.5 Torr, ~10^4 cm s^{-1}). Neutral reactant flow rates were measured by monitoring the pressure change versus time in a calibrated volume system. Reaction rate constants were determined by introducing the neutral reagents at varying distances along the reaction flow tube, thereby varying the reaction distance and time. The $^{35}ClO^-$ intensity was monitored with a quadrupole mass filter coupled to an electron multiplier. Rate constants for the perprotio and perdeuterio reactions were measured sequentially on the same day under the same conditions. The error reported for the reaction rate constants is one standard deviation of three consecutive measurements. The uncertainty due to systematic error is ±20%; however the systematic errors cancel in the rate ratio, and therefore, the KIEs are more accurately determined. Helium buffer gas (99.995%) was purified by passage through a molecular sieve trap at 77 K. Neutral reagents were purchased from commercial sources and used without further purification; however, it was experimentally demonstrated that HCl, which would complicate the results, was not a significant contaminant.[22]

Measured reaction rate constants and deuterium KIEs are reported in Table 1. The reaction of ClO^- with methyl chloride can undergo only an S_N2 reaction, and an inverse KIE of 0.85(±0.01) was measured. This result is consistent with previous measurements of

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Table 1. Experimental Reaction Rate Constants (10^{-10} cm^3 molecule^{-1} s^{-1}) and Deuterium Kinetic Isotope Effects for RCl + ClO^- → Products

RCl	*k*	KIE
CH_3Cl	2.01 ± 0.01	0.85 ± 0.01
CD_3Cl	2.36 ± 0.01	
C_2H_5Cl	2.25 ± 0.01[a]	0.99 ± 0.01[a]
C_2D_5Cl	2.27 ± 0.01[a]	
i-C_3H_7Cl	1.74 ± 0.03	1.72 ± 0.05
i-C_3D_7Cl	1.01 ± 0.02	
t-C_4H_9Cl	2.33 ± 0.03	2.31 ± 0.12
t-C_4D_9Cl	1.01 ± 0.05	

[a] Computational results predict $k = 6.7 \times 10^{-10}$ and $k = 2.8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for ClO^- with C_2H_5Cl and C_2D_5Cl, respectively, and a KIE of 2.4.[1]

inverse KIEs for S_N2 reactions of methyl halides.[23,24] The reaction of ClO^- with *tert*-butyl chloride presumably proceeds primarily by E2.[16] A KIE of 2.31(±0.12) was measured which is consistent with previously measured normal KIEs for E2 reactions.[5,25] As the extent of substitution in the neutral reactants increases, the KIE effects become increasingly more normal. These results indicate that the E2 pathway becomes the dominant channel as the neutral reagent becomes more sterically hindered.

The experimental reaction efficiencies (10% for ClO^- with C_2H_5Cl)[26] and KIE reported here for the reaction of ClO^- with ethyl chloride differ from the theoretical values, suggesting that the S_N2 channel is more prominent than calculations predict. It is difficult to account for the discrepancies between experiment and theory; however nonstatistical dynamics[27] or errors in the calculation of the individual KIE or in the branching ratios of the two channels could account for the discrepancy.

Hu and Truhlar's treatment of the reaction between ClO^- and ethyl chloride assumes that the reaction is statistical. Statistical theories are based on the assumption that energy is randomized among different modes as the reaction proceeds from reactants to the transition state. Nonstatistical effects have been observed for S_N2 reactions of monatomic nucleophiles with methyl halides, and these effects have been extensively documented in the literature.[23,24,28−32] However the use of statistical theories has been successful for slightly larger systems.[33−35] Furthermore, Hu and Truhlar have previously calculated the KIE for the S_N2 reaction of solvated fluoride with methyl chloride using a statistical approach.[36] Their results show excellent agreement with our published experimental values.[37] Thus the assumption that the $ClO^- + C_2H_5Cl$ reaction behaves statistically is reasonable.

The individual KIE values, which Hu and Truhlar evaluated, appear quite reasonable. It can be argued that the errors in the branching ratio calculations are the primary cause for the large deviation from the experimental results.[38] If the predicted branching ratios were correct, the KIE for the E2 channel would need to be 1.0 or smaller or the KIE for the S_N2 channel would need to be 0.13 or smaller to be consistent with the measured overall KIE. These values are not reasonable based on previous results. On the other hand assuming that the individual KIE are correct and that the discrepancy lies in the calculation of the branching ratios, we can use the calculated individual KIE along with the experimental overall rate constant and KIE to predict the rate constants for the S_N2 and E2 channels to be 1.10×10^{-10} cm^3 molecule^{-1} s^{-1} and 1.15×10^{-10} cm^3 molecule^{-1} s^{-1}, respectively, for $ClO^- + C_2H_5Cl$. This analysis suggests that the calculated results overestimate the E2 rate constant by a factor of ∼6 and underestimate the S_N2 rate constant by a factor of ∼2.5. This magnitude of errors would occur if the E2 barrier height was underestimated by only 1 kcal mol^{-1}, while the S_N2 barrier height was overestimated by only 0.6 kcal mol^{-1}. These small deviations in the activation enthalpy can have a large effect on the branching ratios. Determining activation enthalpies with an accuracy of 0.5 kcal mol^{-1} or better is a difficult computational task.[39]

These results illuminate the need for additional studies to describe nucleophilic substitution and elimination reactions more accurately. We hope that the discrepancy between experiment and theory will spark interest for further exploration.

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(22) (CH_3Cl 99.9%, CD_3Cl 99.9%, C_2H_5Cl >99%, C_2D_5Cl 98%, *i*-C_3H_7Cl 99%, *i*-C_3D_7Cl 99.4%, *t*-C_4H_9Cl 99%, *t*-C_4D_9Cl 99.1%). An HCl impurity would complicate the rate measurements due to a rapid proton-transfer pathway, which could not be distinguished from the S_N2 and E2 channels. Therefore, $^{37}Cl^-$ was mass selected and allowed to react with the neutral reagents. We have previously shown [Van Doren, J. M.; DePuy, C. H.; Bierbaum, V. M. *J. Phys. Chem.* **1989**, *93*, 1130] that the rates of these reactions are below the detection limits of our instrument; however, the $Cl^- + HCl$ exchange reaction proceeds at approximately half of the collision rate. The absence of $^{35}Cl^-$ as a product ion indicates that HCl is not a significant contaminant.
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