Deuterium kinetic isotope effects in gas phase S_N2 reactions

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Abstract

Rate coefficients and secondary α-deuterium kinetic isotope effects (KIEs) for the nucleophilic substitution (S_N2) reactions of $Cl^- + CH_3Br \rightarrow CH_3Cl + Br^-$, $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$, $Br^- + CH_3I \rightarrow CH_3Br + I^-$, and their perdeuterated analogs are remeasured in the gas phase at 300 K. The measurements confirm our previous results [Gronert et al., J. Am. Chem. Soc. 113 (1991) 4009] and substantial *inverse* KIEs are measured with an improved accuracy: $k_H/k_D = 0.77$ (± 0.03), 0.84 (± 0.01), and 0.76 (± 0.01), respectively, for the above systems. Thus, the experimentally observed effect of deuterium substitution in these reactions is considerably more dramatic than predicted previously by transition state theory where KIEs are calculated to be closer to unity. The experimental KIE values for the series of S_N2 reactions, F^-, $Cl^- + CH_3Br$ and F^-, Cl^-, $Br^- + CH_3I$ are both found to decrease (i.e. become more *inverse*) with an increase in the transition-state looseness parameter (R_{TS}) for larger halide anions, in contrast to those for lighter methyl halides which show the expected positive correlations with R_{TS}. (Int J Mass Spectrom 210/211 (2001) 223–229) © 2001 Elsevier Science B.V.

1. Introduction

Nucleophilic substitution (S_N2) reactions are one of the most fundamental transformations in organic chemistry, and there have been numerous studies, both experimental and theoretical, on S_N2 processes in the gas phase [1–7]. Secondary α-deuterium kinetic isotope effects (KIEs), defined as the ratio of the S_N2 rate coefficients for nonlabeled (k_H) to deuterium-labeled (k_D) reactants, have been widely used as a sensitive probe for the mechanism of nucleophilic substitution and structure of the S_N2 transition state [8–11]. Whether the KIE is *normal* ($k_H/k_D > 1$) or *inverse* ($k_H/k_D < 1$) is a measure of the available space around the C_α-H(D) bonds and hence of the force field. Poirier et al. devised a transition-state "looseness" parameter (R_{TS}), which is defined as the sum of the lengths of the nucleophile-α-carbon and α-carbon-leaving group bonds at the S_N2 transition state [9]. They have demonstrated computationally that for reactions of CH_3F and CH_3Cl with a variety of nucleophiles, the value of KIE increases from *inverse* ($k_H/k_D < 1$) toward *normal* ($k_H/k_D > 1$) as R_{TS} increases and the transition state becomes looser. Modifications to the looseness parameter have been made that correct for the nucleophile and leaving group atomic
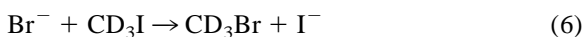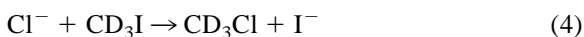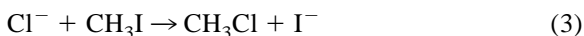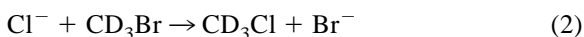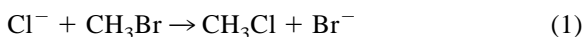
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We are pleased to dedicate this article to Professor Nico Nibbering, an eminent ion chemist and wonderful friend.

radii [10] and three-dimensional "crowdedness" introduced by polyatomic nucleophiles [11].

Despite accumulating knowledge, there still remain discrepancies in the KIEs for fundamental S_N2 reactions. Gronert et al. first reported substantial *inverse* deuterium kinetic isotope effects for the non-identity S_N2 reactions of methyl halides with halide anions [12]

$$Cl^- + CH_3Br \rightarrow CH_3Cl + Br^- \tag{1}$$

$$Cl^- + CD_3Br \rightarrow CD_3Cl + Br^- \tag{2}$$

$$Cl^- + CH_3I \rightarrow CH_3Cl + I^- \tag{3}$$

$$Cl^- + CD_3I \rightarrow CD_3Cl + I^- \tag{4}$$

$$Br^- + CH_3I \rightarrow CH_3Br + I^- \tag{5}$$

$$Br^- + CD_3I \rightarrow CD_3Br + I^- \tag{6}$$

The measured values for KIE were 0.80 [reactions (1) and (2)], 0.84 [reactions (3) and (4)], and 0.76 [reactions (5) and (6)] [12]. Viggiano et al. also measured the deuterium KIE for the $Cl^- + CH_3Br$ reaction in their comprehensive studies on the effects of temperature [13] and temperature/drift field [14] on the reaction kinetics. Hu and Truhlar later conducted extensive computational studies on the KIEs for the above systems [15]. Their analysis based on transition-state theory successfully predicted *inverse* KIEs. The calculated temperature dependence of KIE for the $Cl^- + CH_3Br$ reaction qualitatively agreed with the experimental result [13]. However, the predicted absolute values of KIE are significantly closer to unity than those experimentally determined by Gronert et al. This disagreement is surprising in light of the excellent agreement between theory and experiment for $F^- + CH_3Cl$ [2,9,11] and $F^-(H_2O) + CH_3Cl$ [2,11,16] systems and their deuterated analogs.

In the present study, we remeasure the rate coefficients and KIEs for reactions (1)–(6) in an attempt to resolve the discrepancies between theory and experiment. Impurities in the methyl halide reactants are carefully examined and the effects on the determination of KIE evaluated. The observed kinetic isotope effects are compared to those for nonidentity S_N2

reactions involving lighter methyl halides (CH_3F and CH_3Cl), and the transition-state looseness concept is examined.

2. Experimental

The experiments were carried out using the flowing afterglow selected ion flow tube (FA-SIFT) instrument described previously [17]. Chloride and bromide ions were generated in the source flow tube by electron impact on CCl_4 and C_2H_5Br, respectively. $^{35}Cl^-$ and $^{79}Br^-$ ions were mass selected and injected into the second flow tube with helium carrier gas (0.5 Torr) at 300 K. The helium gas had been prepurified by passage though a molecular sieve trap cooled to liquid nitrogen temperature. Neutral reactants (CH_3Br, CD_3Br, CH_3I, and CD_3I) were introduced into the flow tube at a constant flow rate through a manifold of inlets along the tube. The flow rates were determined by absolute measurement, i.e. monitoring the pressure change with time as the reagent gas fills a calibrated standard volume. Bimolecular reaction rate coefficients were determined from the kinetic decay of parent halide ions as a function of the inlet position and hence the reaction distance [7,17].

In a set of experiments, rate coefficients were measured at least three times for reactions (1)–(6) and results were averaged. Measurements were reproducible to typically within 3% of the mean. Deuterated and corresponding nondeuterated S_N2 reactions were examined very closely in time on the same day and under identical experimental conditions, and KIE values were directly computed. Rate coefficients also include systematic uncertainties (due to calibrations of the helium flow meter, pressure transducer, and thermometer, and assumptions regarding the ion radial distribution, etc.) and the absolute error bars are approximately ±20%. However, KIEs are measured much more accurately as these uncertainties cancel in the ratio of the two rate coefficients. Experiments were repeated over several years by different hands, constituting three independent sets of measurement. Only random fluctuations were observed between the data sets, and values for k_H, k_D, and KIE are reported

Table 1 Rate coefficients (k_H and k_D) and kinetic isotope effects (k_H/k_D) for the S_N2 reactions of halide ions with methyl halides and their perdeuterated analogs

System	k_H (10^{-11} cm^3 s^{-1})	k_D (10^{-11} cm^3 s^{-1})	k_H/k_c[a]	k_H/k_D	Reference
$Cl^- + CH_3Br$	2.58 ($\pm$0.11)[b]	3.33 ($\pm$0.05)[b]	0.012	0.77 ($\pm$0.03)[b]	This work
	2.72 ($\pm$0.14)	3.40 ($\pm$0.19)		0.80 ($\pm$0.06)	[12]
	2.4	. . .		0.81 ($\pm$0.03)	[13]
	2.37	2.68		0.88	[14][c]
	2.37[d]	2.52-2.59[d,e]		0.91-0.94[e]	[15]
$Cl^- + CH_3I$	15.9 ($\pm$0.5)[b]	18.9 ($\pm$0.7)[b]	0.081	0.84 ($\pm$0.01)[b]	This work
	16.6 ($\pm$0.3)	19.8 ($\pm$0.2)		0.84 ($\pm$0.02)	[12]
	16.6[d]	18.3-18.4[d,e]		0.90-0.91[e]	[15]
$Br^- + CH_3I$	2.64 ($\pm$0.18)[b]	3.46 ($\pm$0.23)[b]	0.018	0.76 ($\pm$0.01)[b]	This work
	2.89 ($\pm$0.09)	3.78 ($\pm$0.08)		0.76 ($\pm$0.03)	[12]
	2.88[d]	3.13[d,e]		0.93[e,f], 0.96[g]	[15]

[a] k_c is the parameterized trajectory collision rate [19].

[b] Values are means ($\pm$ one standard deviation) of three independent sets of measurements. Absolute errors for k_H and k_D are approximately 20%.

[c] Table 1 of [14]. Figure 1 of [14] shows $k_H \approx 2.4 \times 10^{-11}$ and $k_D \approx 3.1 \times 10^{-11}$ at 300 K with no drift field, giving $k_H/k_D \approx 0.77$ (see the text).

[d] Rate coefficients ($k = k_{ii} R^{CUS}$) calculated from k_{ii} and R^{CUS} in Table 6 of [15].

[e] Depending on the basis set used (PDZ+ or PTZ+ at the MP2 level of theory).

[f] As in Table 7 of [15].

[g] Higher level of theory (MP4/PDZ+).

as averages ($\pm$1 standard deviation). This uncertainty represents the scatter of the data sets, rather than the error associated with the mean value ($\pm$1$\sigma/\sqrt{3}$), and hence is more conservative.

Methyl halides are obtained from commercial sources with nominal purities of 99.5% (CH_3Br and CH_3I) and 99.5%D (CD_3Br and CD_3I). Impurities in the methyl iodides were further examined by Hauser Chemical Research (Boulder, CO). Molar fractions of hydrogen iodides in CH_3I and CD_3I were assayed as 4.3×10^{-5} and 6.6×10^{-6}, respectively. Iodine was not detected at or above the method detection limit of 5.6×10^{-5}. Probable impurities in methyl bromides are hydrogen bromide and Br_2; hydrogen bromide is presumably the major impurity as it can develop over time through hydrolysis with trace water vapor. The SIFT instrument was used to assay the HBr content in CH_3Br by reacting mass-selected $^{79}Br^-$ with the sample and observing the appearance of $^{81}Br^-$

$$^{79}Br^- + H^{81}Br \rightarrow H^{79}Br + {}^{81}Br^- \qquad (7)$$
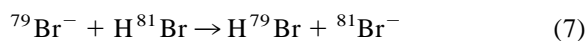
The thermoneutral displacement of $^{81}Br^-$ from naturally occurring hydrogen bromide ($H^{79}Br$:

$H^{81}Br \approx 50:50$) takes place at $\approx$25% of the collision rate whereas the S_N2 counterpart is extremely slow; $Cl^- + CH_3Cl$ is the only identity S_N2 reaction that has ever been accurately measured (reviewed in [18]).

$$^{79}Br^- + CH_3^{81}Br \rightarrow CH_3^{79}Br + {}^{81}Br^- \qquad (8)$$
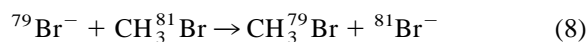
From the assumption that only reaction (7) is accountable for the observed signal of $^{81}Br^-$, an upper limit for the HBr content was estimated as 0.16%. A similar experiment with the CD_3Br sample gave an upper limit for DBr in CD_3Br as 0.22%. Effects of the hydrogen halide impurities on the magnitudes of measured rate coefficients and KIE will be discussed in Sec. 3.

3. Results and discussion

Table 1 summarizes rate coefficients and KIEs determined from the SIFT measurements in this study. Reactions of Cl^- with methyl iodides are more exothermic and moderately rapid ($\approx 10^{-10}$ cm^3 s^{-1}) whereas other reactions are in the range of low 10^{-11}

$cm^3 \, s^{-1}$. High-level G2(+) theoretical calculations predicted the energies of the S_N2 transition states relative to reactants as -2.0, -3.7, and -0.8 kcal/mol for $Cl^- + CH_3Br$, $Cl^- + CH_3I$, and $Br^- + CH_3I$, respectively, at 298 K [20]. Substantial deuterium kinetic isotope effects are observed for these systems with excellent reproducibility: 0.77 (± 0.03) for $Cl^- + CH_3Br$, 0.84 (± 0.01) for $Cl^- + CH_3I$, and 0.76 (± 0.01) for $Br^- + CH_3I$. Hydrogen halide impurities in the neutral reactants have negligible effect on the observed KIE values. Chloride ions react with hydrogen bromide impurities in CH_3Br and CD_3Br at collision rates and will increase the apparent rate coefficients for reactions (1) and (2) by 8.3% and 8.9%, respectively. This results in a reduction of the true value for KIE by ≈ 0.004, well within the uncertainty limits (Table 1). Hydrogen iodides in CH_3I and CD_3I will increase the apparent rate coefficients for reactions (3)–(6) by no more than 0.2% and increase the true values of KIE by less than 0.001, accordingly. The measured rate coefficients and KIEs essentially duplicate our previous study [12] (see Table 1) but with an improved accuracy.

Viggiano et al. used the variable temperature selected ion flow drift tube (VT-SIFDT) to measure the rates and deuterium kinetic isotope effect for the $Cl^- + CH_3Br$ reaction [13]. The reported value of 0.81 (± 0.03) at 300 K is in excellent agreement with both our previous (0.80 ± 0.06) and present (0.77 ± 0.03) studies (Table 1). In a later study, Viggiano et al. investigated the effects of collision energy $\langle KE_{cm} \rangle$ and temperature on the rates and KIE for the same system [14]. At 300 K with no drift field ($\langle KE_{cm} \rangle = 0.039$ eV), Fig. 1 of their article [14] shows $k_H \approx 2.4 \times 10^{-11}$ $cm^3 \, s^{-1}$ and $k_D \approx 3.1 \times 10^{-11} \, cm^3 \, s^{-1}$ giving $k_H/k_D \approx 0.77$, consistent with the above experimental studies. However, in Table 1 of [14], the 300 K value of k_H ($2.37 \times 10^{-11} \, cm^3 \, s^{-1}$) is identical to the data point in Fig. 1 whereas that of k_D is smaller ($2.68 \times 10^{-11} \, cm^3 \, s^{-1}$), giving a larger KIE of 0.88 [14]. In a later theoretical study, Hu and Truhlar discussed their computational values of KIE (0.91–0.94) in comparison with the larger value of Viggiano et al., conclud-
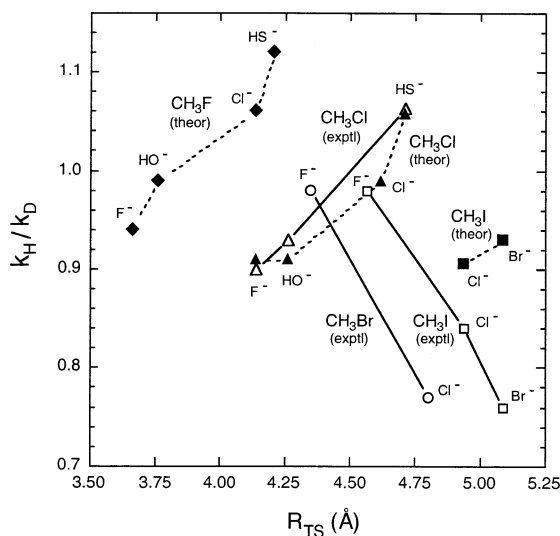

Fig. 1. Experimental (open symbols) and theoretical (closed symbols) KIEs (k_H/k_D) as a function of the transition-state looseness parameter (R_{TS}) [9] for the S_N2 reactions of methyl halides (for CH_3F and CH_3Cl, theory [11]), (for CH_3Cl, experiment [2, 11]; R_{TS} values from theory [11]), (for CH_3Br, experiment [2] and this work; R_{TS} values from theory [20]), (for CH_3I, experiment [2] and this work; the R_{TS} value for F^- from theory [20] and those for Cl^- and Br^- as averages of MP2/PDZ+ and MP2/PTZ+ results [15]), (for CH_3I, theory [15], averages of the MP2/PDZ+ and MP2/PTZ+ results). The level of theory affects both the R_{TS} values and the theoretical k_H/k_D values; however, the observed trends are preserved irrespective of the level of theory. Experimental error bars are not shown for the sake of simplicity; however, they are relatively small and cannot change the observed trends. The dashed and solid lines are intended only to guide the eye.

ing that agreement was good between theory and experiment [15].

The remeasured values of KIE for the $Cl^- + CH_3I$ and $Br^- + CH_3I$ systems are also substantially smaller (more *inverse*) than those predicted by transition state theory [15]. We conclude that the statistical approach of Hu and Truhlar systematically overestimates the KIE values for reactions (1)–(6) (i.e. predicted values closer to unity), in partial disagreement to their interpretation that the theory overestimates the KIE only for the $Br^- + CH_3I$ reaction [15].

In the canonical unified statistical (CUS) model of Hu and Truhlar to calculate the rate coefficients for reactions (1)–(6) [15], the classical barrier heights were adjusted so that the calculated rates agree with

experimental values at 300 K. Therefore, under the framework of transition state theory, the deuterium KIE was calculated from

$$\text{KIE} = \eta_{\text{trans}}\, \eta_{\text{rot}}^{\ddagger}\, \eta_{\text{vib}}^{\ddagger}\, \eta_{\text{var}}\, \eta_{\text{cap}} \qquad (9)$$

where the first three factors correspond to translational, rotational, and vibrational contributions, and the fourth and last factors are contributions from variational effects and capture rates, respectively [15]. The vibrational contribution is given as the double ratio of vibrational partition functions for perprotio to perdeuterio systems

$$\eta_{\text{vib}}^{\ddagger} = \Pi\frac{q_{\text{vib,H}}^{\ddagger}/q_{\text{vib,H}}^{R}}{q_{\text{vib,D}}^{\ddagger}/q_{\text{vib,D}}^{R}} \qquad (10)$$

where $\ddagger$ and R represent the S_N2 transition state and reactant (CH_3X), respectively, and the product is taken over all vibrational modes. The vibrational term was found to be the major factor responsible for the *inverse* KIE for reactions (1)–(6) whereas other terms were nearly constant (either very close to unity or greater than unity) [15]. They examined different sizes of basis sets (PDZ+ versus PTZ+) and levels of theory (MP2 versus MP4) and observed reasonable convergence of vibrational frequencies for both the reactant and transition state [15]. The calculated KIEs, however, are consistently closer to unity than the experimental values from the present study. Both interestingly and disturbingly, calculated values of KIE for the $Br^- + CH_3I$ reaction shifted farther from the experimental value when the higher MP4 level of theory was used (Table 1). A possible explanation for the discrepancy between experiment and theory is the pressure conditions; the calculations of Hu and Truhlar apply to the low pressure limit in which the intermediate complex does not suffer any collisions with third bodies during its lifetime [15]. However, Viggiano et al. examined the effects of helium gas pressure (0.3–0.9 Torr) and observed no difference in the $Cl^- + CH_3Br$ rates at 300 K [14]. A Fourier transform ion cyclotron resonance experiment by Ingemann and Nibbering ($<10^{-5}$ Torr) measured an essentially identical rate coefficient for the same reaction at 300 K [21]. Although an increase by a factor of ≈ 2 was observed for the $Cl^- + CH_3Br$ rate at a much higher pressure (640 Torr of nitrogen, 308 K) [22], the S_N2 rates and hence KIEs for the present systems do not appear to be significantly affected by pressure under SIFT conditions in the present study. The Rice-Ramsperger-Kassel-Marcus (RRKM) lifetime (after correction for anharmonicity) for the $[Cl^- \cdots CH_3Br]$ complex formed by collision of Cl^- with CH_3Br at 300 K is approximately 10 ps [23], several orders of magnitude shorter than the collision interval with helium (≈ 100 ns) under the present experimental conditions.

Not only are the experimental KIEs for $Cl^- + CH_3Br$, $Cl^- + CH_3I$, and $Br^- + CH_3I$ farther from unity than those theoretically predicted, but S_N2 reactions involving CH_3Br and CH_3I exhibit reversed trends in KIEs with respect to the looseness parameter, R_{TS}. Fig. 1 shows correlations between the KIE and R_{TS} for S_N2 reactions of small nucleophiles reacting with methyl halides CH_3X (X = F, Cl, Br, and I). Monatomic (F^-, Cl^-, and Br^-) and small diatomic (HO^- and HS^-) nucleophiles are chosen so that the correlation is minimally disturbed by the additional crowdedness factor [11]. Other experimental KIEs are taken from our previous SIFT measurements [2,11]. Different levels of theory have been used for calculating R_{TS} values (and also computational KIEs based on the transition state approach), i.e. MP2/6-31++G** [11], MP2/6-31+G(*d*) [20], and MP2/PDZ+ and MP2/PTZ+ [15]. Nevertheless, all data are displayed on the same graph since structures and vibrational frequencies are relatively insensitive to these reasonably high levels of theory [24]. This approach does not affect the qualitative trends in Fig. 1. Computational KIEs for both CH_3F and CH_3Cl reactants correlate positively with R_{TS} at MP2/6-31++G** [11]. A similar trend had been observed earlier by Poirier et al. at the HF/6-31+G* level of theory [9]. Experimental KIEs for CH_3Cl substantiate the computational predictions (Fig. 1). In clear contrast, experimental KIEs for CH_3Br decrease with an increase in the looseness parameter in going from F^- to Cl^- (Fig. 1). A similar steep decrease was observed for CH_3I reacting with F^- to Cl^- to Br^-. The reversed trends in these heavier methyl halide reactions seem

to remain valid even if the largest observed KIEs with F^- (0.98 ± 0.02 for F^- + CH_3Br and 0.98±0.05 for F^- + CH_3I [2]) have nearly saturated to unity because of their high reaction efficiencies ($k_H/k_c = 0.71$ and 0.77, respectively) [25]. Interestingly, transition-state theory still predicts a positive correlation between the KIEs for Cl^-, Br^- + CH_3I and the looseness parameter (Fig. 1).

Poirier et al. have demonstrated that among the vibrational modes contributing to the $\eta^\ddagger_{vib}$ [Eq. (10)], the C−H bending modes are the most significant factors for determining the trend of $\eta^\ddagger_{vib}$ and hence the overall KIE with respect to the looseness parameter [9]. For the S_N2 reactions of CH_3F and CH_3Cl, strong positive correlations similar to those in Fig. 1 are observed between the partial KIE for the bending modes ($\eta^\ddagger_{bend}$) and R_{TS} [9]. A similar positive correlation was observed in higher-level calculations (MP2/6-31++G**), which factored in out-of-plane bending modes [11]. We calculate the values of $\eta^\ddagger_{bend}$ for Cl^- + CH_3I and Br^- + CH_3I reactions using the vibrational frequencies reported by Hu and Truhlar [15], with the classical zero of energy taken as the zero of energy. For the out-of-plane C−H umbrella mode, the values of $\eta^\ddagger_{bend}$ are 1.062 and 1.073 for Cl^- + CH_3I and Br^- + CH_3I, respectively. Corresponding values for the doubly degenerate out-of-plane C−H bending mode are 0.843 and 0.849. (The above values are from averages of the MP2/PDZ+ and MP2/PTZ+ frequencies [15].) The slightly positive correlation with respect to R_{TS} once again fails to account for the reversed trend observed experimentally. A modified looseness parameter [10] may present a more quantitative correlation for these systems with larger halogen atoms; however, this will not affect the disagreement between experiment and the transition-state approach.

Viggiano et al. showed in their VT-SIFDT study [14] that for a fixed relative translational energy $\langle KE_{cm}\rangle$, the S_N2 rate for Cl^- + CH_3Br does not depend on the temperature (vibrational/rotational energy) of CH_3Br, a result inconsistent with RRKM theory [26]; this approach assumes randomization of energy within the ion–molecule collision complex and predicts rate coefficients to be dependent on the total

energy of the system, not specifically on translational or vibrational energy. No effect of additional vibrational excitation in neutral reactants has been found for any S_N2 reaction of halide ions with methyl halides studied so far, whereas S_N2 reactions of non-methyl halide systems behave statistically [27]. This difference is considered to be a consequence of the extremely short lifetimes for the collision complexes of halide anions with methyl halides; energy randomization is not accomplished within the time scale of the complex dissociation. In a trajectory study on the Cl^- + CH_3Br collision at 300 K, Wang et al. found the (harmonic) RRKM lifetime of the $[Cl^- \cdots CH_3Br]$ complex to be extremely short ($\approx$3 ps) [23]. Within the $[Cl^- \cdots CH_3Br]$ collision complex, energy transfer is incomplete between the high-frequency intramolecular modes (in the CH_3Br moiety) and low-frequency intermolecular modes (between Cl^- and CH_3Br). They predicted that S_N2 dynamics of this reaction is vibrational-mode specific and hence nonstatistical; excitation of the CH_3Br intramolecular modes in the $[Cl^- \cdots CH_3Br]$ complex assists central barrier crossing on the S_N2 double-minimum potential energy surface, leading to the nucleophilic substitution products (CH_3Cl+Br^-). On the other hand, excitation of the intermolecular modes leads to back-dissociation of the complex (Cl^-+CH_3Br) [23]. Recently, Tonner and McMahon generated the stable $[Cl^- \cdots CH_3Br]$ complex and vibrationally excited this species with different infrared sources [28]. They observed exclusive production of Br^- by excitation of the high-frequency modes in the $[Cl^- \cdots CH_3Br]$ complex (by way of continuous wave CO_2 laser irradiation) whereas the Cl^- product arises from low-frequency excitation (by way of blackbody infrared radiation) [28], consistent with the previous theoretical prediction. S_N2 reaction rates of F^- with CH_3Br and CH_3I, including that with CH_3Cl, were also found to be independent of internal energy [27]. These results suggest that KIEs for the CH_3Br and CH_3I systems (Fig. 1) are better described by a model taking non-statistical dynamics into account, rather than by the statistical model employing the partition function relationships. Wang and Hase examined several statistical theories for the Cl^- + CH_3Br

reaction, and showed that those theories failed to predict the dependence of the rate coefficient on temperature, translational energy, and isotope substitution (one model predicted k_H/k_D to be 0.79 at the harmonic level, but agreement was lost when anharmonic frequencies were used) [29]. The KIE value for $F^- + CH_3Cl$ [2], however, agrees well with the prediction by transition state theory [9,11]. Further theoretical studies will be required to fully understand the S_N2 dynamics and KIE behaviors for these heavy methyl halide systems.

4. Conclusions

Remeasured rate coefficients and α-deuterium KIEs for the nonidentity S_N2 reactions duplicate our previous measurements. The KIE values are not affected by trace impurities in the reactants, and they are consistently smaller (more *inverse*) than those predicted by the statistical model of Hu and Truhlar. The experimental KIEs for the F^-, $Cl^- + CH_3Br$ and F^-, Cl^-, $Br^- + CH_3I$ reactions decrease with an increase in the looseness parameter of Poirier et al., in contrast to those for CH_3F and CH_3Cl reactions which show expected positive correlations for a variety of nucleophiles. The observed decrease in KIE in going from $Cl^- + CH_3I$ to $Br^- + CH_3I$ is also contradictory to the prediction based on the looseness concept. These results on KIEs present further theoretical challenges for detailed understanding of the dynamics of S_N2 reactions.

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