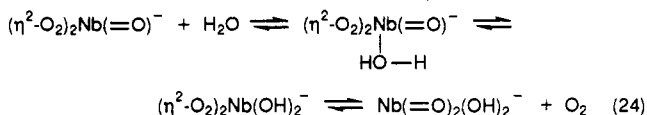


and product ions in eqs 18-23 have exactly six bonds to the Nb central atom. Perhaps the only way for there to be six bonds to Nb in  $\text{NbO}_5^-$  is to have two sideways bound  $\text{O}_2$  molecules and one doubly bound oxygen atom.  $\text{MoO}_5$  in  $\text{MoO}_5(\text{HMPT})(\text{Py})$  and  $\text{MoO}_5(\text{HMPT})(\text{H}_2\text{O})$  is characterized by crystallography<sup>28</sup> as having two dihapto sideways bound  $\text{O}_2$  molecules and one doubly bound O atom, i.e.,  $(\eta^2\text{-O}_2)_2\text{Mo}(=\text{O})(\text{HMPT})(\text{Py})$  and  $(\eta^2\text{-O}_2)_2\text{Mo}(=\text{O})(\text{HMPT})(\text{H}_2\text{O})$ . In addition<sup>28</sup> the HMPT ligand is bound by means of an oxygen atom provided by HMPT, and pyridine (Py) is N atom bound while  $\text{H}_2\text{O}$  is presumably O atom bound to the metal center. Therefore,  $\text{NbO}_5^-$  may be  $(\eta^2\text{-O}_2)_2\text{Nb}=\text{O}^-$  (a 12-electron complex).

Table I and eq 8 reveal that reactions such as that of  $\text{TaO}_5^-$  ( $\text{NbO}_5^-$ ) with  $\text{H}_2\text{O}$  can be run in reverse under appropriate conditions. Dioxygen added to  $\text{TaO}_2(\text{OH})_2^-$  gives back  $\text{TaO}_5^-$  and  $\text{H}_2\text{O}$ . A mechanism for this reversible reaction that reflects the concepts expressed here is illustrated for niobium in eq 24.



For reaction with  $\text{H}_2\text{O}$ , the oxygen atom of the water molecule datively coordinates to the metal atom of the pentoxide anion followed by migration of a proton from HOH to form another OH group. Thereafter, this is followed by loss of a dihapto- $\text{O}_2$  molecule and conversion of  $\text{Nb}(\eta^2\text{-O}_2)$  to  $\text{Nb}(=\text{O})_2$ . Again, the actual structures are unknown, but the ones described here are consistent with the evidence. The reaction proceeds in the other direction by oxidative sideways addition of  $\text{O}_2$  to  $\text{Nb}(\text{OH})_2(\text{OH})_2^-$ . Note that  $(\eta^2\text{-O}_2)_2\text{Nb}(=\text{O})(\text{H}_2\text{O})^-$  is analogous to  $(\eta^2\text{-O}_2)_2\text{Mo}(=\text{O})(\text{HMPT})(\text{H}_2\text{O})$ .

#### IV. Conclusions

Negatively charged oxides and oxyhydroxides of tantalum, niobium, vanadium, and tungsten were produced, and their

properties and reactivity were investigated. In contrast to the niobium and tantalum cases, tungsten oxide anions demonstrated no reactivity toward  $\text{H}_2\text{O}$ . Reaction with  $\text{O}_2$  was observed to occur 2-3 orders of magnitude slower ( $k \approx 10^{-11}$ - $10^{-13} \text{ cm}^3 \text{ s}^{-1}$ ), in general, than the  $\text{H}_2\text{O}$  reactions that proceed. A reversible reaction was observed to occur between the dioxydihydroxide and pentoxide anions for both niobium and tantalum, and an equilibrium constant was calculated from the ratio of the forward and reverse rate coefficients in each case. Sequential reactions were observed for HCl reacting with niobium and tantalum oxide (and oxyhydroxide) anions. Interestingly, these reactions bear analogy to condensed-phase acid-base interactions along the line of NaOH and HCl reacting to give NaCl and  $\text{H}_2\text{O}$ . For the transition metal oxide anions, Cl of HCl replaces an OH unit on the metal center and  $\text{H}_2\text{O}$  is the neutral product. When there are no OH units bonded to the metal atom, HCl adds to form an OH unit and a Cl unit bonded to the metal center with no neutral reaction product being released. Rate coefficients, varying from about  $10^{-9}$  to  $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , were determined for each of four sequential additions of HCl for both the niobium and the tantalum systems. Mechanisms are proposed which utilize dative-coordination, as well as oxidative-addition/reductive-elimination concepts for the formation and decay of the transitory reaction intermediates for each reaction step. In the future, it will be desirable to expand this work to include other negatively charged metal oxide reactants such as oxides of titanium, chromium, and rhenium. Also it should be feasible to study the reactivity of the anions which have two or more metal atoms. A larger number of neutral reactant gases could be used in all of these studies to further probe the nature of the oxide.

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## Kinetics of the Gas-Phase Reactions of $\text{Cl}^-$ with $\text{CH}_3\text{Br}$ and $\text{CD}_3\text{Br}$ : Experimental Evidence for Nonstatistical Behavior?

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**Abstract:** The reactions of  $\text{Cl}^-$  with  $\text{CH}_3\text{Br}$  and  $\text{CD}_3\text{Br}$  have been studied as a function of ion-neutral average center-of-mass kinetic energy,  $\langle \text{KE}_{\text{cm}} \rangle$ , at several temperatures. The reactions are inefficient, proceeding at only a few percent of the collision rate. Both increasing temperature and increasing kinetic energy are found to decrease the rate constant as approximately  $T^{-0.8}$  or  $\langle \text{KE}_{\text{cm}} \rangle^{-0.8}$ . The rate constants were found to be independent of pressure at 300 K. At a fixed  $\langle \text{KE}_{\text{cm}} \rangle$ , no dependence of the rate constants on temperature was found. This indicates that the rate constants for the reactions do not depend on the internal temperature of the  $\text{CH}_3\text{Br}$  or  $\text{CD}_3\text{Br}$ . By comparison with other systems, we conclude that rotational excitation of the  $\text{CH}_3\text{Br}$  should have little effect on the rate constants. Combining the apparent lack of a rotational dependence and the fact that significant amounts of the  $\text{CH}_3\text{Br}$  or  $\text{CD}_3\text{Br}$  molecules are vibrationally excited leads to the conclusion that the rate constants are also not strongly dependent on vibrational energy.

#### Introduction

Bimolecular nucleophilic displacement ( $\text{S}_{\text{N}}2$ ) is one of the most basic types of chemical reaction. For this reason, numerous studies have been made to elucidate the dynamical details of the mechanism.<sup>1-37</sup> In contrast to many other types of gas-phase ion-molecule reactions, nucleophilic displacement reactions are often

slow.<sup>38</sup> There has been speculation that the inefficiency results from the reaction coordinate being a double well, i.e., two ion-

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molecule complexes separated by a chemical barrier.<sup>7,8</sup> At long range the reactants are attracted and form the reactant complex. The inefficiency is a result of the competition between reaction (passage over the chemical barrier) and dissociation back into reactants (passage over the centrifugal barrier). The magnitude of the rate constant is often predicted by statistical theories, such as RRKM theory.<sup>8,39</sup>

The existence of both the entrance and exit channel complexes has been recently established by several research groups, and the two complexes have been shown to be different.<sup>34,37</sup> However, several recent studies have called into question the ability of statistical theories to describe the reactivity. DePuy et al.<sup>4</sup> have postulated that the central barrier does not affect the reactivity in systems for which the efficiency is on the order of 50%. Su et al.<sup>6</sup> have shown that orientation effects should be considered in  $S_N2$  reactions. Hase and co-workers<sup>18-21</sup> have used trajectory calculations to show that the symmetric  $S_N2$  reaction of  $Cl^-$  with  $CH_3Cl$  displays nonstatistical behavior. Most recently, Graul and Bowers<sup>35</sup> and VanOrden et al.<sup>36</sup> have shown that the kinetic energy releases in  $S_N2$  reactions display nonstatistical behavior.

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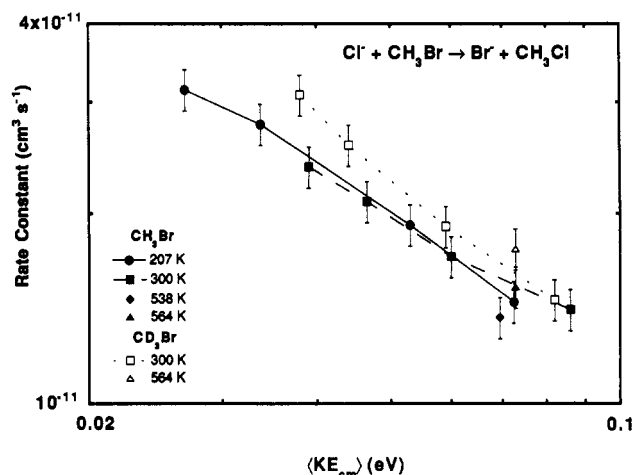
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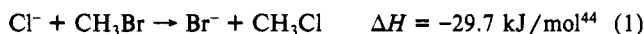


**Figure 1.** Rate constants for the reactions of  $Cl^-$  with  $CH_3Br$  and  $CD_3Br$  as a function of  $\langle KE_{cm} \rangle$  at several temperatures. Solid points refer to  $CH_3Br$  and open points refer to  $CD_3Br$ . Circles, squares, diamonds, and triangles refer to temperatures of 207 K, 300 K, 538 K, and 564 K, respectively. Lines are given for convenience only.

**Table I.** Rate Constants for  $Cl^-$  Reacting with  $CH_3Br$  and  $CD_3Br$  at 300 K

rate constant ( $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ )		technique <sup>a</sup>
$CH_3Br$	$CD_3Br$	
$2.37 \pm 0.6$	$2.68 \pm 0.7$	SIFDT (this work)
$2.72 \pm 0.5$	$3.40 \pm 0.7$	SIFT <sup>3,4</sup>
2.5		HPMS <sup>39</sup>
$2.6 \pm 0.2$		FTICR <sup>50</sup>
$2.1 \pm 0.1^b$		FA <sup>14</sup>
1.2		ICR <sup>8</sup>
$1.7 \pm 0.4$		FA <sup>12</sup>

For systems that behave statistically, the rate constants will depend on the total energy and angular momentum of the system and not specifically on vibrational or translational energy.<sup>40</sup> We have recently developed a technique for determining separately the effects of translational and internal energy on rate constants or branching ratios for ion-molecule reactions.<sup>41-43</sup> This technique therefore should provide insight into whether reactions behave statistically. We report here rate constant measurements as a function of temperature, kinetic energy, and internal temperature of  $CH_3Br$  for the reaction of  $Cl^-$  with  $CH_3Br$ :



and its deuterated analogue,  $CD_3Br$ .

## Experimental Section

The measurements were made using the Phillips Laboratory (formerly the Geophysics Laboratory) variable-temperature-selected ion flow drift tube apparatus.<sup>43</sup> Instruments of this type have been the subject of review,<sup>45</sup> and only those aspects important to the present study will be discussed in detail.  $Cl^-$  was made in an electron impact ion source from  $CF_2Cl_2$ . The ions were extracted from the source, mass selected in a quadrupole mass filter, and injected into a flow tube through an orifice surrounded by a Venturi inlet through which the helium buffer gas was added.  $CH_3Br$  was added through one of two downstream inlets, and rate constants were measured in the standard manner.<sup>43,46</sup> Pressure in the

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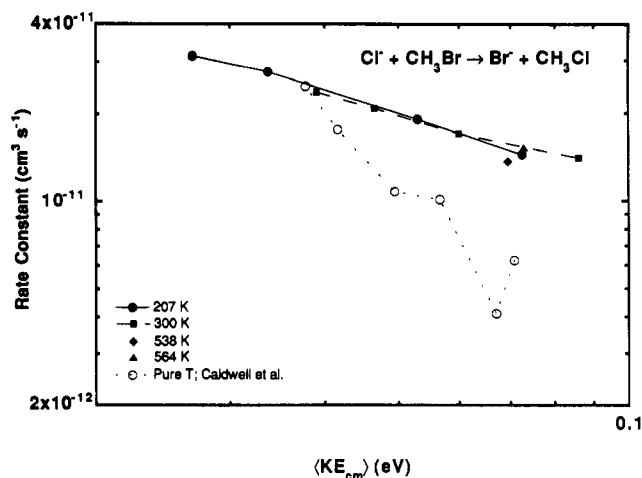
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**Figure 2.** Rate constants for the reaction of  $\text{Cl}^-$  with  $\text{CH}_3\text{Br}$  as a function of  $\langle \text{KE}_{\text{cm}} \rangle$ . Solid points refer to the present data and open circles refer to the data of Caldwell et al.<sup>39</sup> Circles, squares, diamonds, and triangles refer to temperatures of 207 K, 300 K, 538 K, and 654 K, respectively. Lines are given for convenience only.

experiments was on the order of 0.5 Torr. Relative and absolute uncertainties are estimated to be  $\pm 15\%$  and  $\pm 25\%$ , respectively.<sup>43</sup> The  $\text{CD}_3\text{Br}$  was obtained from Cambridge Isotope Laboratory and is  $\geq 99.5\%$  isotopically pure.

A drift tube is positioned inside the flow tube, and the entire flow tube can be heated or cooled. Rate constants can therefore be measured as a function of temperature and ion kinetic energy. The average kinetic energy in the ion-neutral center-of-mass system,  $\langle \text{KE}_{\text{cm}} \rangle$ , in the drift tube is derived from the Wannier formula<sup>47</sup> as

$$\langle \text{KE}_{\text{cm}} \rangle = \frac{(m_i + m_b)m_n}{2(m_i + m_n)} v_d^2 + \frac{3}{2} kT \quad (2)$$

where  $m_i$ ,  $m_b$ , and  $m_n$  are the masses of the reactant ion, buffer gas, and reactant neutral, respectively;  $v_d$  is the ion drift velocity; and  $T$  is the temperature. A given average center-of-mass kinetic energy,  $\langle \text{KE}_{\text{cm}} \rangle$ , is obtained with varying contributions of the temperature term and the drift tube term. Comparing rate constants at a particular  $\langle \text{KE}_{\text{cm}} \rangle$  but with varying contributions from the two terms yields the dependence of the rate constant on the internal temperature of the reactant neutral (if the ion is monatomic, as in the present study).<sup>41,42</sup>

## Results and Discussion

The rate constants measured for reaction 1 are shown in Figure 1. More data were obtained for  $\text{CH}_3\text{Br}$  than for  $\text{CD}_3\text{Br}$  because of the high cost of  $\text{CD}_3\text{Br}$ . The reactions are inefficient, proceeding in only a few percent of all collisions.<sup>48,49</sup> Drift field data were not obtained above room temperature because the rate constants were too small to be measured with the same precision as the data reported. Rate constants with larger uncertainty could be obtained at elevated energies but would be harder to interpret. To be conservative, we stopped taking data when results from the complete temperature range could be compared at least at one kinetic energy.

The present room-temperature rate constants are compared with previous measurements in Table I. The agreement is generally very good, with one of the ICR values being somewhat low. Excluding that value, the average is  $2.3 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ , in good agreement with the present value. The rate constant for  $\text{CD}_3\text{Br}$  has been measured previously in one other experiment, and the agreement is also good. The kinetic isotope effects measured in the two experiments are in good agreement and are discussed elsewhere.<sup>3,25</sup> Both increasing temperature and increasing kinetic

energy are found to decrease the rate constant as approximately  $T^{-0.8}$  or  $\langle \text{KE}_{\text{cm}} \rangle^{-0.8}$ .

The temperature dependence of reaction 1 has also been examined in a high-pressure mass spectrometry experiment (HPMS).<sup>39</sup> Our data are compared with the HPMS temperature dependence in Figure 2. Temperature has been converted to  $\langle \text{KE}_{\text{cm}} \rangle$  by  $\langle \text{KE}_{\text{cm}} \rangle = (3/2)kT$ . Good agreement is found at low temperature (300 K = 0.039 eV), but at high temperatures the HPMS rate constants are considerably lower than the present ones. It is relatively difficult to make this large an error (up to a factor of 4) in our experiment. For every data point, we measure all parameters that are needed to measure a rate constant, i.e., temperature, pressure, reaction time, flow rate, concentration, and ion signals.<sup>43,46</sup> The presence of impurities in the  $\text{CH}_3\text{Br}$  is the only potential problem which is likely to cause our rate constants to be erroneously large to this extent. This seems to be unlikely for several reasons. (1) Impurity levels would need to be relatively high. Assuming that the impurity reacted at the collisional rate, the impurity level would need to be the order of 1%. If it reacted more slowly, then a higher concentration of impurity is required to explain the discrepancy. (2) The good agreement between the  $\text{CH}_3\text{Br}$  and  $\text{CD}_3\text{Br}$  data would mean that the impurity levels in the two reagents would be the same, and this also seems unlikely at the levels needed. (3) The good agreement between our data and numerous others at room temperature indicates that impurities do not play a major role at room temperature or below (since the rate constants are larger at lower temperature). (4) For impurities in our experiment to be the cause of the difference at high temperature, approximately two-thirds of the reactivity would be due to impurities. Assuming that the impurity reacted at the collision rate (which, as stated above, requires a rather high impurity level), then little temperature dependence would be expected in the part of the rate constant due to impurities. This would imply that our low-temperature rate constants would have to be lowered by 40%, causing us to disagree with previous measurements. (5) If the measured rate constants were due in large part to an impurity reacting at the collision rate, the rate constants would be expected to flatten out at higher temperature/energy. This is not observed experimentally. (6) A recent study<sup>51</sup> of this reaction at 398 K and atmospheric pressure indicates that the rate constant is  $3.4 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ . This value is more in line with our value than with the HPMS value, although it is larger than the present results. However, this rate constant was obtained at high pressure, and the discrepancy with the present results may be due to a three-body effect in the atmospheric pressure data.

On the other hand, the HPMS data are scattered at high temperature.<sup>39</sup> At low temperature, the rate constant decreases fairly smoothly with roughly a 40–60% decrease for each 60 K of temperature increase. Above that point large deviations are seen. From 390 K to 450 K only a 7% decrease is seen. From 450 K to 530 K a decrease of 145% is seen. Finally, over the narrow temperature range of 530 K to 560 K an increase of 34% is observed. Real variations in rate constants for ion–molecule reactions are rarely, if ever, this large.<sup>38</sup> Especially troubling is the large decrease from 450 K to 530 K followed by an appreciable increase from 530 K to 560 K. This scatter indicates a problem in the HPMS measurements. The source of the problem is unclear. The only possibility apparent to us is that the source of the  $\text{Cl}^-$  in the HPMS experiments is in the reaction zone, and production of  $\text{Cl}^-$  after the initial electron pulse by secondary chemistry would cause the rate constants to be erroneously low. A possible source of  $\text{Cl}^-$  could be an associative detachment reaction of an impurity ion with  $\text{CH}_3\text{Br}$ , followed by rapid electron attachment to  $\text{CCl}_4$ , the source gas for  $\text{Cl}^-$ . This is in contrast to our experiments where the  $\text{Cl}^-$  source is separate from the reaction region. For the above reasons, we assume that our results are correct.

Caldwell et al.<sup>39</sup> speculated on the possibility that the rate constants are in part controlled by interaction of the reactant complex with the buffer gas. In order to check this possibility,

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**Table II.** Rate Constants for  $\text{Cl}^-$  Reacting with  $\text{CH}_3\text{Br}$  as a Function of Pressure

pressure (Torr)	rate constant $\text{CH}_3\text{Br}$ ( $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ )
0.3	2.43
0.42	2.47
0.9	2.43

we have studied the reaction as a function of pressure at 300 K and no drift electric field over as wide a pressure range as was practical in our instrument. The results are listed in Table II. No pressure dependence was found under these conditions. If the complex is interacting with the buffer, this interaction does not appear to affect the rate constant. At higher temperature and energy conditions this should still apply (the complex lifetime becomes shorter). Therefore, the interaction between the helium buffer and the complexes does not affect our derivation of internal energy dependences.

Additional information comes from comparing the 300 K rate constants measured using different apparatuses. This allows comparison over a very wide pressure range (from  $5 \times 10^{-7}$  Torr to several Torr). The rate constant data taken at high pressure (0.3 Torr and higher, i.e., the flow tube and HPMS data) average to  $2.27 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . The two ICR values measured at very low pressure ( $\sim 10^{-6}$  Torr) disagree. One value is considerably lower than the above average, and the other is in good agreement. There is reason to be suspicious of the low value since the rate constants for reactions of  $\text{CH}_3\text{Br}$  reported in that paper are significantly lower than those reported elsewhere in four out of five  $\text{CH}_3\text{Br}$  reactions measured.<sup>38</sup> If the lower number is in error as suspected, then the rate constants are pressure independent over a very wide range. Since lifetimes of the intermediate complexes will decrease with increasing temperature, we would also expect that this pressure independence pertains to temperatures above 300 K as well. The results of Giles and Grimsrud<sup>51</sup> indicate that the buffer gas may influence the reaction at much higher pressure.

Graul and Bowers<sup>55</sup> found that some unknown fraction of  $\text{Cl}^-$ - $\text{CH}_3\text{Br}$  complexes decay in a time window of 5–10  $\mu\text{s}$ . In our apparatus the time between collisions with the buffer is on the order of 0.1  $\mu\text{s}$ . The absence of a pressure effect in the rate constants and the long lifetime may appear to be in conflict. However, comparing the two experiments is difficult. Most likely only a small fraction of the complexes were detected in Graul and Bowers work since their signal levels were low. In addition, these workers believe that the complexes they detect have been partially stabilized in the ion source since they see signals only at elevated source pressures. This comparison is therefore inconclusive, and we cite the lack of pressure dependence as evidence that buffer collisions with the complex do not affect our results.

The negative temperature and energy dependences are typical of ion-molecule reactions. Various theoretical treatments of negative temperature dependences of rate constants for ion-molecule reactions have been published.<sup>6,52–56</sup>

The dependence of the rate constants on the internal temperature of  $\text{CH}_3\text{Br}$  (or  $\text{CD}_3\text{Br}$ ) is obtained by comparing rate constants at the same  $\langle \text{KE}_{\text{cm}} \rangle$  but at different temperatures.<sup>41,42</sup> At a given  $\langle \text{KE}_{\text{cm}} \rangle$ , the relative contributions of temperature and drift field to eq 2 vary with the temperature of the buffer gas. Upon examining Figure 1, it can be seen that, within our relative experimental uncertainty ( $\pm 15\%$ ), no dependence on temperature at the same  $\langle \text{KE}_{\text{cm}} \rangle$  is observed for either reaction at any  $\langle \text{KE}_{\text{cm}} \rangle$ . Note that data covering the entire temperature range exist only at  $\sim 0.07 \text{ eV}$ , but the lack of a temperature dependence at a

**Table III.** Ground-State Fraction of Various Vibrational Modes of  $\text{CH}_3\text{Br}$  and  $\text{CD}_3\text{Br}$  at Three Temperatures, Calculated Using the Harmonic Oscillator Assumption<sup>a</sup>

frequency (cm <sup>-1</sup> )	temperature			mode description
	207 K	300 K	564 K	
CH <sub>3</sub> Br				
2972	1.00	1.00	1.00	C-H stretch
1305	1.00	1.00	0.96	umbrella
611	0.99	0.95	0.79	C-Br stretch
3056 (2)	1.00	1.00	1.00	C-H stretch
1443 (2)	1.00	1.00	0.90	twist
954 (2)	0.99	0.96	0.68	twist
total $\nu = 0$	0.98	0.90	0.47	
CD <sub>3</sub> Br				
2151	1.00	1.00	1.00	C-H stretch
987	1.00	0.99	0.92	umbrella
577	0.98	0.94	0.77	C-Br stretch
2293 (2)	1.00	1.00	0.99	C-H stretch
1053 (2)	1.00	0.98	0.75	twist
717 (2)	0.97	0.88	0.49	twist
total $\nu = 0$	0.95	0.80	0.25	

<sup>a</sup>Degeneracies are in parentheses. Frequencies are taken from Herzberg.<sup>69</sup>

particular  $\langle \text{KE}_{\text{cm}} \rangle$  is found at lower  $\langle \text{KE}_{\text{cm}} \rangle$  over smaller temperature ranges. The lack of dependence of the rate constant on temperature at a fixed kinetic energy means that increasing the internal energy leaves the rate constant unchanged.

The lack of a dependence on the internal temperature of  $\text{CH}_3\text{Br}$  can be interpreted in one of two ways. The first is that neither rotational nor low-frequency vibrational modes (the only ones excited at the temperatures of these experiments; see Table III) affect the reactivity to a large degree. Alternatively, several effects could cancel. For instance, rotational excitation could decrease the rate constant and vibrational excitation could increase it. It should be noted that we define rotational excitation as the rotational angular momentum of  $\text{CH}_3\text{Br}$  and not the orbital angular momentum of the collision. We do this because the orbital angular momentum is the same when comparing data at the same center-of-mass kinetic energy.

Using the technique described in this paper, we have previously obtained information on the effect of rotational angular momentum on the rate constant for 14 systems.<sup>6,41–43,46,57–64</sup> In 12 of these systems, the effect of rotational angular momentum was 20% or less over temperature ranges comparable to or larger than that used in the present experiments. For those systems that showed a small effect, it was always found that increasing temperature decreased the rate constant slightly. In the two other systems, both of which were charge-transfer reactions, larger dependences were observed. The reasons for the larger dependences,<sup>43,59,63</sup> namely, endothermicity and large dipole moment of the neutral, do not pertain to the present system. To the best of our knowledge, information on rotational energy dependences is available for only three other bimolecular ion-molecule systems.<sup>65–67</sup> The only one that shows a rotational effect is also due

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to endothermicity.<sup>65</sup> In at least two of the above systems, the minimum potential energy pathway is known to be similar to that for reaction 1,<sup>46,68</sup> i.e., a double minimum with the barrier just below the zero of energy. In all of these systems, the only positive dependences on rotational excitation are in endothermic reactions. We therefore conclude that rotational angular momentum is unlikely to have a large effect on the rate constant for reaction 1, and any effect is likely to be negative. Consequently, vibrational excitation is also unlikely to have a large effect.

Table III lists the fractions of  $\text{CH}_3\text{Br}$  and  $\text{CD}_3\text{Br}$  that remain in the ground vibrational level at the temperatures of our experiments. At low temperatures almost all of the  $\text{CH}_3\text{Br}$  and  $\text{CD}_3\text{Br}$  molecules are in the ground vibrational level. At higher temperatures, over half of the  $\text{CH}_3\text{Br}$  and three-quarters of the  $\text{CD}_3\text{Br}$  molecules have at least one quantum of vibrational excitation, and significant levels of overtone excitation are also present. Our sensitivity is such that, if the rate constant for vibrationally excited  $\text{CH}_3\text{Br}$  or  $\text{CD}_3\text{Br}$  were 30% different from that for  $v = 0$ , we would be able to detect the difference. This statement assumes a population weighted average rate constant for vibrational excitation and no dependence on rotational temperature.

The two vibrational modes that might be expected to have the largest effect on the reactivity are the umbrella mode and the C-Br stretch. These are the two modes that could be expected to couple directly into the reaction coordinate, since the standard mechanism involves a Walden inversion of the  $\text{CH}_3$  group (umbrella) followed by the  $\text{Br}^-$  leaving (C-Br lengthening). Less than 10% of the molecules are excited in the umbrella mode at high temperature, but the C-Br stretch is excited in over 20% of both  $\text{CH}_3\text{Br}$  and  $\text{CD}_3\text{Br}$  molecules. If the C-Br stretch increased the rate constant by a factor of 1.7, we could detect it, again assuming no rotational dependence. We have observed much larger vibrational enhancements for other systems using the same technique.<sup>46,61</sup>

In statistical theories, rate constants are assumed to depend only on total energy and total angular momentum since these are conserved quantities.<sup>40</sup> Specifically, statistical theories do not distinguish between whether energy is supplied as translational or vibrational energy except to the extent that translational energy affects the orbital angular momentum. Our data show that increasing translational energy decreases the rate constants. While some of the decrease may be due to the changes in orbital angular momentum associated with changing translational energy, it is still likely that translational energy decreases the rate constants since this is typical behavior for ion-molecule reactions.<sup>38</sup> Increasing the sum of rotational and vibrational energy leaves the rate constant unchanged. We have argued that rotational excitation is unlikely to have much of an effect on the rate constants (at a fixed  $\langle \text{KE}_{\text{cm}} \rangle$  and therefore fixed orbital angular momentum) and that if it does play a role it is likely to decrease the rate constant slightly. Taken together, these last two statements then indicate that vibrational excitation of the low-frequency modes of  $\text{CH}_3\text{Br}$  is likely either to leave the rate constants unchanged or to increase them slightly. Thus, our data indicate that vibrational energy and translational energy probably have different effects on the rate constants for reaction 1. Therefore, if our conclusions are correct that (1) rotational excitation of  $\text{CH}_3\text{Br}$  either leaves the rate constants unchanged or decreases them slightly and (2) translational energy decreases the rate constants even after taking into account orbital angular momentum changes, then our data indicate that the rate constants cannot be described by statistical theories such as RRKM theory. This would be a

test of one of the fundamental assumptions of these theories rather than the implementation of them, but our test is subject to interpretation.

In concluding that reaction 1 behaves nonstatistically, we include the possibility that the nonstatistical nature of the reactivity is in the entrance channel, although the evidence given below makes it unlikely that entrance channel effects can completely account for the present observation. While for a number of years it was assumed that statistical theories could be used to model gas-phase  $\text{S}_{\text{N}}2$  reactions,<sup>8,39</sup> a number of experiments have recently called this into question. In previous work in our laboratory<sup>6</sup> on reactions of  $\text{F}^-$  with  $\text{CH}_3\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), we found similar results to those reported here, i.e., rate constants that decreased with increasing temperature/kinetic energy and rate constants that did not depend on temperature at a given  $\langle \text{KE}_{\text{cm}} \rangle$ . Trajectory calculations<sup>6</sup> indicated that at least part of the dependence of  $\langle \text{KE}_{\text{cm}} \rangle$  could be explained by orientation effects. The rate constants for those reactions are considerably larger than those reported here, and the lack of a temperature dependence at a given  $\langle \text{KE}_{\text{cm}} \rangle$  was attributed mainly to a lack of sensitivity; i.e., the rate constants approached (but did not reach) the collisional rate constant, and therefore little internal temperature dependence was expected. In light of the present results, however, we believe the lack of internal dependence is more fundamental.

Recently, Graul and Bowers<sup>35</sup> have examined the kinetic energy release distribution of metastable  $\text{Cl}^- \cdot \text{CH}_3\text{Br}$ . They found that the fraction of the released energy that is partitioned into internal excitation of the  $\text{CH}_3\text{Cl}$  product is significantly greater than that predicted from a statistical theory. Van Orden et al.<sup>36</sup> have also found nonstatistical distributions of the product energy in the reaction of  $\text{F}^-$  with  $\text{CH}_3\text{Cl}$ . Examining differences in reactivity in a series of reactions, DePuy et al.<sup>4</sup> have postulated that the central barrier does not affect the reactivity for systems where the efficiency is on the order of 50%.

Probably the most insightful studies into the dynamics of  $\text{S}_{\text{N}}2$  reactions are the trajectory calculations by Hase and co-workers<sup>18-22</sup> on the symmetric reaction of  $\text{Cl}^- + \text{CH}_3\text{Cl}$ . Their results also indicate non-RRKM behavior as well as a number of other interesting observations. Of particular importance to the present results is that they find that "the rate constants for the initial 80% of the complex's dissociation are consistent with intramolecular vibrational energy redistribution between the three low-frequency "intermolecular" modes formed as  $\text{Cl}^-$  and  $\text{CH}_3\text{Cl}$  associate, with no (or negligible) energy transfer to/from the vibrational modes of  $\text{CH}_3\text{Cl}$ . Thus, the lifetime of the complex which predominantly decomposes to reactants is not significantly affected by the number of quanta in the C-Cl stretch."<sup>22</sup> The independence of the rate constant on vibrational energy found in the present study is consistent with this interpretation; i.e., excitation of the low-frequency vibrational modes in  $\text{CH}_3\text{Br}$  does not couple into the reaction coordinate. In the studies by Hase and co-workers, multiple crossings of the central barrier occurred, which also indicates nonstatistical behavior.

## Conclusions

While it has been shown that simple  $\text{S}_{\text{N}}2$  reactions do proceed along a reaction coordinate with two wells, several experiments have shown that at least some of these reactions behave nonstatistically. The present experiments do not rely on calculations to come to this conclusion, although they do rely on several assumptions. It should be mentioned, however, that the present results cannot rule out the possibility that the nonstatistical nature of the reactivity is in the entrance channel. The abundance of other data on similar systems would appear to preclude this possibility from being the sole source of the effect we have observed.

Essentially all of the evidence for nonstatistical behavior involves systems of monatomic ions reacting with simple halomethanes. An interesting question is whether the nonstatistical nature of these reactions is a result of the size of the systems. Nonstatistical behavior should be more prevalent in small systems. As the number of modes increases, the easier it is for energy to travel

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throughout all the modes, since the density of states increases. For instance, the only known example of selective bond breaking in a bimolecular reaction by vibrational mode selectivity is the reaction of H with HOD, where a local mode picture of the OH and OD bonds is warranted.<sup>70,71</sup> For larger molecules the local

mode picture breaks down, and energy is transferred more efficiently. More work of the type presented here and elsewhere is needed to determine whether S<sub>N</sub>2 reactions involving larger ions and molecules will also show nonstatistical behavior.

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## Alkyl Substituent Effects in Cyclopentadienyl Metal Complexes: Trends in Gas-Phase Ionization and Electron Attachment Energetics of Alkylnickelocenes

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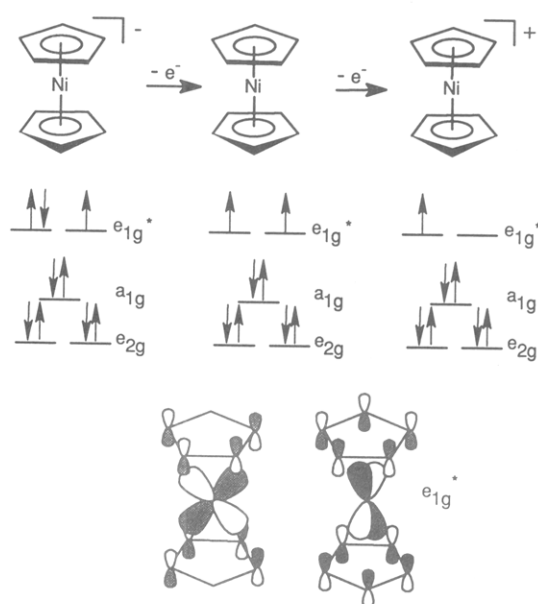
**Abstract:** Electron-transfer equilibrium (ETE) methods have been used to establish the gas-phase ionization and electron attachment energetics for nickelocene and several alkylated derivatives, (RCp)(R'Cp)Ni (R, R' = H, Me, Et, *t*-Bu). The nickelocene derivatives were highly purified by reversed-phase HPLC, and ETE studies were performed on a Fourier transform ion cyclotron resonance mass spectrometer. The results are summarized as free energies of ionization ( $\Delta G_i^\circ$ ) and free energies of electron attachment ( $\Delta G_a^\circ$ ) at 350 K for the (RCp)(R'Cp)Ni<sup>0/+</sup> and (RCp)(R'Cp)Ni<sup>0/-</sup> couples, respectively. The order of ionization energies follows the expected trend, with more and larger alkyl substituents leading to decreasing values of  $\Delta G_i^\circ$ . The  $\Delta G_a^\circ$  values become more endoergic as methyl groups are substituted, but larger alkyl groups lead to more exoergic electron attachment as the size of the alkyl substituents increases. Alkyl substituent effects cannot be described as uniformly "electron donating" in these redox processes and must be rationalized on the basis of more detailed models. As an example, a model based on a combination of inductive and polarization effects is used to analyze the data. Alternative single-parameter correlations with published substituent parameters are also considered. The average differential solvation free energy for the Cp<sub>2</sub>Ni<sup>+/0</sup> and Cp<sub>2</sub>Ni<sup>0/-</sup> couples in THF is estimated from the gas-phase data and the difference in the solution electrode potentials ( $\Delta\Delta G_{\text{solv,av}}^\circ = -39 \pm 3 \text{ kcal mol}^{-1}$ ).

### Introduction

Alkyl substituent effects have been studied extensively in organic chemistry with an emphasis on acidities, basicities, and reactivity in carbon compounds.<sup>1</sup> It has been recognized that *intrinsic* substituent effects are best determined in gas-phase experiments that remove the influence of solvation, which can significantly modify the intrinsic effects.<sup>1,2</sup> Relatively few gas-phase studies of alkyl substituent effects in the chemistry of metal complexes have appeared<sup>3-5</sup> and little is known about intrinsic alkyl effects in the thermochemistry of metal complex redox couples.

On the basis of the results of photoelectron<sup>4,5</sup> and electrochemical<sup>6</sup> studies, it is commonly assumed that alkyl groups on

Scheme I



metal complex ligands are "electron-donating" in metal complex redox processes (i.e., stabilizing the oxidized form relative to the reduced form). In order to explore the nature of alkyl substituent effects in transition metal compounds further, we have used

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