

COMMUNICATIONS

Electron transfer to oriented molecules: Surprising steric effect in *t*-butyl bromideSean A. Harris^{a)} and Philip R. Brooks^{b)}*Chemistry Department and Rice Quantum Institute, Rice University, Houston, Texas 77251*

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Collisions between neutral K atoms and oriented *t*-butyl bromide molecules produce the ions K^+ and Br^- at energies high enough to separate charged particles (≥ 4 eV). Ions are detected by coincidence of mass spectrometry for orientation of the *t*-butyl bromide such that the K atom attacks either the Br end or the *t*-butyl end of the molecule. At high energies the steric asymmetry factor is larger than that for CH_3Br . But at energies near threshold, the steric asymmetry factor reverses sign and attack at the *t*-butyl end becomes **more** reactive than attack at the Br end. The electron is apparently transferred into different orbitals at different ends. © 2001 American Institute of Physics. [DOI: 10.1063/1.1380233]

I. INTRODUCTION

Chemical reactivity is assumed to be site-specific, a concept introduced ≈ 400 B.C. by Democritus who suggested that different “atoms” had different shapes. Modern spectroscopy and kinetics reinforce this notion of course, as do recent experiments in which reagents have been oriented in space prior to collision. The number of reports is still small, but virtually every chemical process has been shown to depend on reagent orientation: chemical reaction,^{1,2} electron transfer,³ ionization,^{4–6} scattering from surfaces,⁷ orientation changes,^{8,9} and light absorption.¹⁰

We recently examined the effect of molecular orientation on electron transfer to CH_3Br in collisions with neutral K atoms.¹¹ This is a “harpoon” reaction in which the neutral reagents approach on a covalent surface but encounter a crossing with an ionic surface, and the electron is adiabatically transferred from the K to the CH_3Br . At thermal energies, there is not enough energy to separate the charges, and some further reaction must occur (i.e., formation of KBr). By raising the initial energy we can separate the nascent ions and can directly study the electron transfer.^{12–14} CH_3Br was chosen as an initial test because we expected (and found) that only Br^- would be formed. The Br end was more reactive.

Systematic variation of the target suggests studying *t*- C_4H_9Br , which is expected to be more hindered than CH_3Br (see inset to Fig. 3). Since *t*- C_4H_9Br , is more of an oblate top than CH_3Br , it can be better oriented and steric effects might approach 100%. Although the actual steric effect is large, it *reverses sign* at low energies and the alkyl end becomes more reactive. At low energies the electron is apparently transferred into an orbital located at the alkyl end. At higher energies this channel apparently closes, making the Br end more reactive as is usually assumed.

II. EXPERIMENT

The apparatus has been described earlier.^{11,15,16} Collisions between neutral reagents occur in the intersection of a seeded beam of *t*- C_4H_9Br (typically 90% He, 5% *t*- C_4H_9Br , and 5% SF_6), and a hyperthermal (5–20 eV) beam of K atoms. The fast atoms are formed in a charge-exchange oven and the beam intensity drops sharply at low energies due to space charge effects.¹⁷ The supersonic gas beam is state-selected in a 1400 mm hexapole field without beam stops, and a weak beam is transmitted even if no voltage is applied to the hexapole. Energizing the hexapole focuses or defocuses symmetric top molecules such as CH_3Br or *t*- C_4H_9Br , depending on their quantum state. Molecules in states with positive Stark effects (the energy increases with field) are repelled by the rods and focused, whereas molecules in negative Stark states are attracted by the rods and defocused. The focused intensity is drawn from large initial solid angles and greatly surpasses the diminution caused by defocusing. Thus the intensity of symmetric top molecules increases when the field is energized, whereas the intensity of nonpolar molecules such as SF_6 is unchanged.

The beams cross inside a separately pumped ultra high vacuum chamber ($\approx 10^{-8}$ Torr) midway between two time-of-flight (tof) mass spectrometers arranged along a line lying roughly along the relative velocity. One tof unit is biased to collect negative ions and the other to collect positive ions, or vice versa. A weak field (≈ 300 V/cm) between the detectors lies roughly along the relative velocity and provides a quantization axis for the molecules.

The state selected symmetric top molecules make adiabatic transition (the quantum numbers remain the same) from the high voltage field of the hexapole to the uniform field between the detectors where they are oriented with respect to the laboratory.³ Interchanging the potentials on the tof mass spectrometers reverses the direction of the uniform field and consequently the lab orientation. Relays under computer

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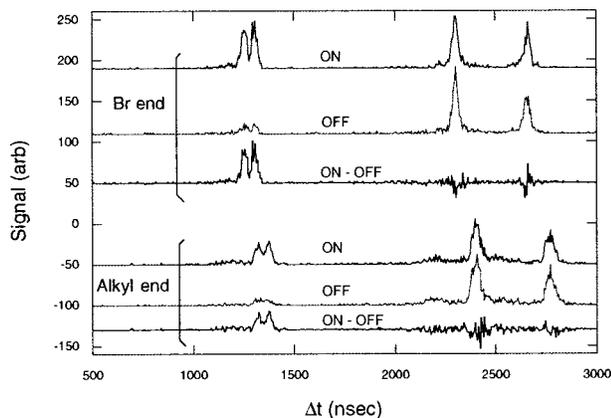


FIG. 1. Coincident time-of-flight spectra for 5.4 eV (CM) K atoms colliding with a seeded beam containing SF_6 and *t*-butyl bromide. On/off denotes hexapole on/off with analyzing of mass spectrometers in either negative end or positive end attack. Mass peaks near 2300 and 2700 ns are due to SF_5^- and SF_6^- , respectively. Since SF_6 is not focused by the hexapole, the high voltage on/off signal difference essentially eliminates these signals. The peaks near 1300 ns are due to Br^- from *t*- $\text{C}_4\text{H}_9\text{Br}$, which is focused by the hexapole and oriented in the collision, giving a net difference signal due to oriented *t*-butyl Br molecules.

control switch the potentials and signals to make comparison between orientations.

III. RESULTS

Coincidence time-of-flight mass spectra are acquired for hexapole on and hexapole off, each in the orientation corresponding to attack at the negative end or positive end of the molecule. The orientation is determined by the direction of the electric field at the reaction center, which in turn is determined by the polarity of the tof detectors. For negative end attack, the tof detector nearest the K oven is biased negatively to collect positive ions. The mass spectra are *coincidence* spectra: each count represents a K^+/X^- pair. Since the beams are continuous and the voltages are constant, there is no time zero. But the ions are formed simultaneously and we measure the time *difference* between the arrival of the K^+ and the negative ion X^- . The time difference depends on the initial velocities of the ions and is reflected in slightly different Δt 's in different orientations. SF_6 provides mass and energy calibration as well as detector normalization for the two orientations.

Figure 1 shows that negative end attack of *t*- $\text{C}_4\text{H}_9\text{Br}$ is more reactive than positive end attack, although the peaks must be integrated to account for different peak shapes. We conclude that at 5.4 eV attack at the Br end is much more likely to produce the Br^- ion than attack at the alkyl end, similar to the behavior of CH_3Br .

The cross section for reaction increases with collision energy so the magnitude of the negative-end and positive-end signals also increase with collision energy. In order to clearly display the effect of orientation on the reaction process, we calculate the *steric effect*, G , as

$$G = [R_B - R_A] / [R_B + R_A],$$

$$\text{where } R_{B,A} = [\Delta S / \Sigma \text{SF}_6]_{B,A},$$

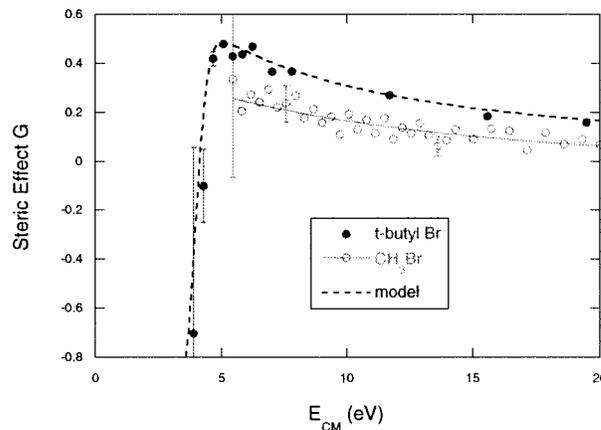


FIG. 2. Steric effect for *t*- $\text{C}_4\text{H}_9\text{Br}$ and CH_3Br . Representative error bars are shown for low energies and are smaller than symbols at higher energies. Small variations in steric effect are not considered significant. Dashed line is a model fit described in text.

where ΔS is the Br^- signal difference between hexapole on and off, ΣSF_6 is the *sum* of the SF_5^- and SF_6^- ion intensities with hexapole on and off, and B or A correspond to Br end or alkyl end attack. The Br^- signals are referenced to the sum of the SF_6 ion signals to account for different detection and collection efficiencies in the two orientations. SF_6 is not influenced by the hexapole, the weak electric field at the reaction center is not expected to influence the reactivity, and ΣSF_6 should be the same in the two orientations. G is thus the *difference* in reactivity for positive end or negative end attack divided by the reactivity sum. If reaction occurs only at one end, $G = \pm 1$ and if both ends are equally reactive, $G = 0$.

The steric effect is shown in Fig. 2 in comparison to that for CH_3Br . As expected, at energies above about 5 eV, the steric effect for *t*- $\text{C}_4\text{H}_9\text{Br}$ is significantly larger than that for CH_3Br and decreases with energy. But the most striking and unexpected comparison between the two molecules is that for *t*- $\text{C}_4\text{H}_9\text{Br}$, the steric effect decreases at low E and appears to change sign!

In order to resolve whether the relative reactivity increases at the alkyl end or decreases at the Br end, we have examined the raw Br^- signals in the two orientations. At low energies the raw Br^- signals show that alkyl-end attack becomes *more* reactive at low energies. To account for variation in beam intensities, we also normalized the signals to either the sum of the SF_6 signals or the Br^- HV off signal. (The Br^- HV off signal is due to truly randomly oriented *t*- $\text{C}_4\text{H}_9\text{Br}$ molecules and is thus independent of "orientation".) Each method leads to the same conclusion: the relative reactivity at the alkyl end **increases** as the energy is lowered. Figure 3 shows $\Delta S/\text{HV}_{\text{off}}$ vs energy for the two orientations. While signals for negative-end attack vary smoothly as the energy is lowered, the signals for alkyl end attack show a dramatic rise at lower energies and the alkyl end becomes relatively more reactive than the Br end.

IV. DISCUSSION

The steric effect and the difference signals indicate that two mechanisms lead to formation of the K^+/Br^- pair.

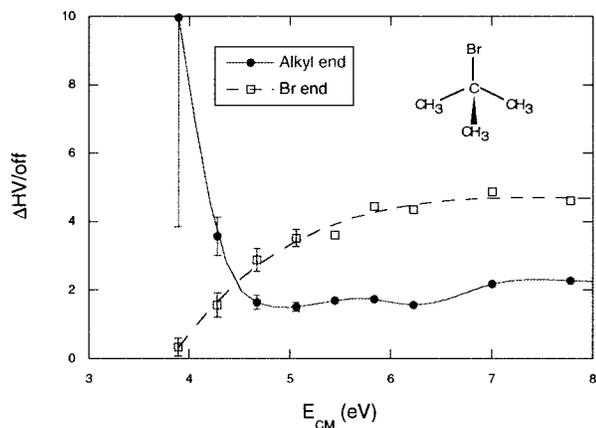


FIG. 3. Hexapole difference signals normalized to hexapole off signals for alkyl end attack and Br end attack. A few representative error bars are shown, and smooth curves are drawn through the points. Inset shows structure of *t*-butyl Br.

Mechanism I (low energies) favors attack at the alkyl end of the molecule but diminishes above ≈ 4 eV in comparison to mechanism II favoring attack at the Br end.

The steric effect in Fig. 2 can be fit with the following ad hoc model; assume that excitation function for I rises from a threshold \mathcal{E}_1 but dies off exponentially above a critical energy, \mathcal{E}_c to account for channel II opening at a second threshold, \mathcal{E}_2 ,

$$\sigma_n = 0 \quad \text{for } E < \mathcal{E}_n \quad (n = \text{I, II}),$$

$$\sigma_n = a_o(E - \mathcal{E}_n) + b_o(E - \mathcal{E}_n)^2 \quad \text{for } E \geq \mathcal{E}_n$$

$$(n = \text{I, II}; o = \text{Br or alkyl attack}),$$

$$\sigma_I = \{a_o(E - \mathcal{E}_1) + b_o(E - \mathcal{E}_1)^2\} \exp[-c(E - \mathcal{E}_c)]$$

$$\text{for } E \geq \mathcal{E}_c,$$

where a_o and b_o depend on orientation. The threshold for each mechanism is orientation independent,¹¹ but I (alkyl end attack) has a lower threshold and dies off above the threshold for II (Br end attack). The overall excitation function is $\sigma_I + \sigma_{II}$. The parameters shown in Table I produce the ‘fit’ shown in Fig. 2. These parameters are sensitive mainly to the threshold energies \mathcal{E}_n , and show that this model is reasonable.

A. Attack at the Br end

Mechanism II, Br end attack at higher energies, occurs for both CH_3Br and *t*- $\text{C}_4\text{H}_9\text{Br}$, presumably via electron transfer into the C–Br σ^* orbital. The nascent molecular ion is most likely formed in the geometry of the neutral, corresponding to a region on the repulsive wall of the anion, and is expected to dissociate into a radical and the Br^- ion.

TABLE I. Model parameters.

Mechanism	a (l^2/eV)		b (l^2/eV) ²		\mathcal{E}_c (eV)
	Br-end	R-end	Br-end	R-end	
I	0	15	0	10	1.5
II	10	2	0.9	0.95	3
$\mathcal{E}_c = 3.5$ eV; $c = 4$ (eV) ⁻¹					

Thermal energy reaction of K atoms with oriented CH_3I and *t*- $\text{C}_4\text{H}_9\text{I}$ showed that more KI is formed if the I end of the molecule is attacked.¹⁸ At thermal energies (and a little higher¹⁹) the only channel available is salt formation because the ions cannot escape the Coulomb attraction. Reaction is observed at the I (or Br) end, apparently because of the proximity of the ions. If the energy is increased enough to form ions but near the threshold for ion production, as is the case here, there may be a lingering tendency for Br end attack to still produce the salt, resulting in a small Br^- ion signal. As the energy is raised beyond threshold, the ions would be more likely to escape from one another, and the Br end signal would rise, behaving qualitatively as shown in Fig. 3.

B. Attack at the alkyl end

This ‘backside’ approach is not favored for thermal reaction to produce salt molecules,¹⁸ perhaps because the K^+ and Br^- (or I^-) would be on opposite sides of the molecule. At energies slightly above thermal, but below the threshold for ion production, $\text{K} + t\text{-C}_4\text{H}_9\text{I}$ gives a bimodal energy distribution for the KI salt, which is postulated to arise from different modes of attack, with alkyl end attack perhaps yielding an excited *t*- C_4H_9 radical.¹⁹

But alkyl end attack is preferred for ion production in *t*- $\text{C}_4\text{H}_9\text{Br}$, at energies near the ion formation threshold. We have also observed alkyl end attack in reaction of oriented CH_3CN . In that case the very stable radical anion CH_2CN^- is formed preferentially upon attack at the CH_3 end of the molecule, whereas CN^- is formed preferentially by attack at the CN end.¹⁶ Methyl bromide might be expected to behave similarly, but it has not so far been possible to extend those observations to lower energies.

In both CH_3CN and *t*- $\text{C}_4\text{H}_9\text{Br}$, the electron appears to be transferred into an alkyl orbital at the ‘back’ end of the central carbon atom. The electron could be transferred into a C–H or C–C orbital to form a temporary molecular negative ion different from that produced if the electron were transferred into the C–Br orbital. As shown in Fig. 3, alkyl-end reactivity for *t*- $\text{C}_4\text{H}_9\text{Br}$ decreases as the energy is increased, or equivalently, as the collision duration decreases. While charge migration to the Br would be rapid compared to the collision duration, a geometrical change would be comparable to the collision duration and may be necessary to produce Br^- . Thus if the collision duration is too short the geometry change would not occur, and electron could be transferred back to the alkali.

At very low energies the Br^- channel must close because the ions cannot be separated. Electron transfer to the alkyl might yield the parent molecular negative ion, which we have tentatively identified in other (unoriented) experiments at lower energies.²⁰ Thus as the energy is decreased, Br^- may disappear in favor of *t*- $\text{C}_4\text{H}_9\text{Br}^-$ formed preferentially by alkyl end attack, consistent with a lower activation barrier predicted for backside $\text{S}_{\text{N}}2$ reactions.²¹ If the energy increases, reactivity at the alkyl end is certainly dwarfed by Br end attack, or as this model suggests, alkyl end attack might be quenched by the electron being transferred back to the incoming K and there being no net reaction.

V. SUMMARY

Electron transfer to *t*-C₄H₉Br produces Br⁻ mainly by Br-end attack at energies above ≈5 eV. Below that energy, the preferred geometry changes and attack at the *t*-C₄H₉ end becomes dominant. Electron transfer to the alkyl group might produce a transient molecular negative ion. If this ion requires a geometry change before the Br⁻ ion is released, ion production might be quenched by back electron transfer which is expected to be more rapid. At sufficiently low energy the channel to form Br⁻ is closed and this molecular negative ion might be stable.

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