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# Evidence for Preferential Electron Transfer to the Br End of Oriented CF$_3$Br

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Although electron transfer is common in many chemical and biological processes, unresolved questions arise concerning pathways[1,2] for intramolecular electron transfer and which molecular sites can accept an electron. We report here direct evidence of preferential electron transfer to one end of a simple prototypical molecule, CF$_3$Br, chosen because it can be oriented in a molecular beam.[3-5] Either the Br end or the CF$_3$ end can be presented for attack by a potassium atom from an intersecting beam, and K$^+$ reaction product ions are detected at collision energies of $\approx$4 eV. Ionization is always more favored for attack at the Br end, and the energetic thresholds for ion formation are different: 3.4 (Br end) and 4.0 eV (CF$_3$ end). Below 4 eV, ionization is observed *only* for attack at the Br end of the molecule, and in this energy range only the parent[6] CF$_3$Br$^-$ ion is formed.

Ion-producing collisions of K atoms with simple molecules (CH$_3$Br and CF$_3$Br) oriented in a molecular beam have been previously studied[7] to provide insight into the electron-transfer process and its dependence on the orientation of the acceptor molecule. For both molecules, more ions were produced when K was incident on the Br end, even though the Br end is negative in CH$_3$Br. Interpretation of these observations is complicated because the collision energy ($\approx$10 eV) was sufficient to fragment the molecular anion and the likely products were K$^+$, Br$^-$, and CF$_3$ (or CH$_3$). With the third body (CF$_3$ or CH$_3$) available to conserve momentum, the positive and negative ions can emerge from the collision travelling either parallel or antiparallel, depending on the initial orientation of the molecule. The relative direction of the ions influences the likelihood of escape as ions, and these exit channel interactions alone were sufficient to explain the orientation behavior of the *overall* reaction consisting of the electron jump, the anion decomposition, and the ion escape.[8] Because of these strongly orientation-dependent exit channel interactions in the previous studies, no conclusions could be drawn regarding the orientation dependence of the initial electron transfer.

We report here measurements showing that thresholds to produce K$^+$ ions are orientation dependent: 3.4 eV for attack at the Br end and 4.0 eV for attack at the CF$_3$ end. In contrast to the earlier experiments, only K$^+$ and CF$_3$Br$^-$ are formed at these low energies, and the strongly orientation-dependent interactions in the exit channel are absent. The orientation effect thus mainly reflects formation of the ions, and the electron appears to be preferentially transferred to the Br end of the molecule. Even though these observations are made at energies of a few electronvolts, we believe that they are characteristic of electron transfer processes at lower, thermal energies as well.

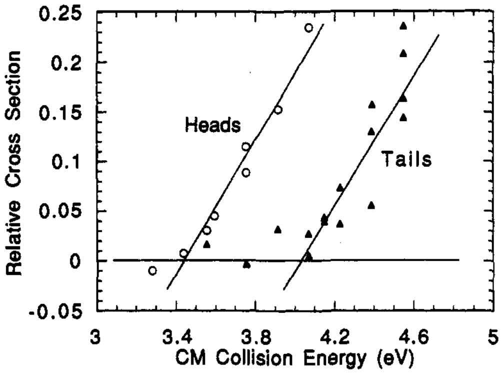

**Figure 1.** Relative cross sections for heads and tails orientations for the K + CF$_3$Br reaction near threshold for ion production. The energy is determined ($\pm\approx$0.2 eV) by mechanical modulation and time of flight of the beams.[10] Thresholds of unoriented SF$_6$ (3.73 eV, not shown) are in good agreement with those of Compton et al.[15]

Electron transfer can be experimentally observed if the kinetic energy of collision is greater than the Coulombic attraction, allowing the ion pair to separate as individual ions. To provide this kinetic energy, beams of fast K atoms are generated by charge exchange[9] and intersect with helium-seeded beams of CF$_3$Br which have been passed through a combination of electrostatic fields to filter out "wrong" molecular orientations.[3-5] The collision occurs in a weak electrostatic field which can be reversed in direction to present either the positive end or the negative end to the incoming atoms. Positive ions formed in the collision are detected by one or the other of two channeltron particle multipliers[10] and counted. For details, see refs 8 and 10.

The "oriented" molecules comprise a collection of quantum-state selected molecules,[11] each precessing about a spatially-defining weak electric field, analogous to the precession of a child's top about the gravitational field. Reversing the direction of the weak field reverses the orientation of the molecules. In CF$_3$Br, for example, comparison is between "Br end" and "CF$_3$ end", corresponding classically to looking down on the precessing tops or up through the floor. To emphasize that the experimental comparison is between two sets of orientation distributions, analogous to the two sides of a coin, the nomenclature "heads" and "tails" is used, where heads represents the end of the molecule with the weaker C–X bond. These orientations have a dramatic effect upon reactivity as shown earlier.[7,8] For CF$_3$Br, the positive (Br) end of the molecule is always observed to be more reactive than the negative end.

Considerably higher signal/noise and extensive averaging ($\approx$30 min/point) now establish that the kinetic energy thresholds for K + CF$_3$Br are orientation dependent. As shown in Figure 1, heads has a lower threshold, and, in the energy range 3.4–4.0 eV, reaction occurs *exclusively* at the heads (Br) end of the molecule.

The minimum energy required to produce fragments K$^+$, Br$^-$, and CF$_3$ is 4.04 eV; below this energy, the only negative ion produced[6] is the parent, CF$_3$Br$^-$. Thus, below 4.04 eV, the reaction produces only two particles, K$^+$ and CF$_3$Br$^-$, which must leave

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(1) Moser, C. C.; Keske, J. M.; Warncke, K.; Farid, R. S.; Dutton, P. L. *Nature* **1992**, *355*, 796–802.

(2) Beratan, D. N.; Onuchic, J. N.; Winkler, J. R.; Gray, H. B. *Science* **1992**, *258*, 1740–1741.

(3) Brooks, P. R. *Science* **1976**, *193*, 11–16.

(4) Stolte, S. In *Atomic and Molecular Beam Methods*; Scoles, G., Ed.; Oxford: New York, **1988**; Vol. 1, pp 631–652.

(5) Parker, D. H.; Bernstein, R. B. *Annu. Rev. Phys. Chem.* **1989**, *40*, 561–595.

(6) Compton, R. N.; Reinhardt, P. W.;Cooper, C. D. *J. Chem. Phys.* **1978**, *68*, 4360–4367.

(7) Harland, P. W.; Carman, H. S., Jr.; Phillips, L. F.; Brooks, P. R. *J. Phys. Chem.* **1991**, *95*, 8137–8142.

(8) Harland, P. W.; Carman, H. S., Jr.; Phillips, L. F.; Brooks, P. R. *J. Chem. Phys.* **1990**, *93*, 1089–1097.

(9) Helbing, R. K. B.; Rothe, E. W. *Rev. Sci. Instrum.* **1968**, *39*, 1948–1950.

(10) Xing, G. Ph.D. Thesis. Rice University, Houston, TX, **1993**.

(11) Each molecule selected has $\langle \cos\theta \rangle < 0$, where $\theta$ is the angle between the precessing dipole moment and the applied field. (also see refs 3–5). For the collection of molecules studied, computer simulations predict $\overline{\cos\chi}$ for the oriented molecules is $\approx -0.4$, where $\chi$ is the angle between the velocity of the incident K atom and the dipole moment of the top. (For unoriented molecules, $\overline{\cos\chi} = 0$.) Xing, G.; Kasai, T.; Brooks, P. R., in preparation. See also: Brooks, P. R. *J. Phys. Chem.*, **1993**, 97, 2153–2157.

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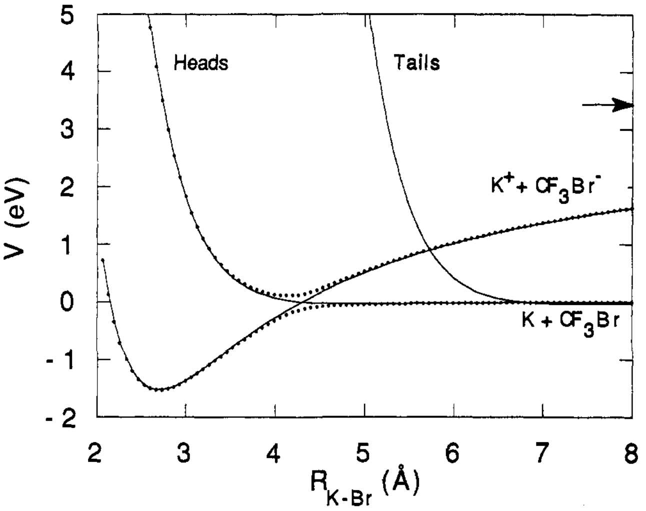

**Figure 2.** Approximate (one-dimensional) ionic and covalent diabatic potentials adapted from ref 16 for $CF_3Br$. Heads and tails are covalent curves, and the ionic curve is a Rittner-type potential for parent ions. The ionic asymptote is denoted by an arrow. The crossings are avoided; dotted curves for the "crossing" near 4.3 Å are the adiabatic curves resulting from configuration interaction[17] between the diabatic ionic and covalent curves. (Adiabatic curves for the other crossing are omitted for simplicity.)

the collision travelling in opposite directions to conserve momentum. The strongly orientation-dependent three-body exit channel interactions, which were adequate to explain the high-energy (≈10 eV) orientation behavior, are therefore absent. Effects of orientation between 3.4 and 4.0 eV must arise mostly from the electron transfer in the entrance channel, and we conclude that for energies near threshold, the electron is transferred preferentially to the Br end of the molecule.

The electron probably jumps to an antibonding $p\sigma^*$ orbital composed largely of p orbitals from carbon and bromine,[12] which is expected to be more accessible from the Br end of the molecule. The threshold results show that transfer through the $CF_3$ end is apparently impeded by a barrier of about 0.6 eV (14 kcal/mol), which can be overcome by increasing the collision energy, resulting in fragmentation of the anion. This is qualitatively illustrated by the potential curves in Figure 2, where the covalent potential for tails approach includes an extra repulsion term to account for the $CF_3$ group interposed between the K and Br. This extra repulsion forces the tails orientation crossing to be at larger distances (and higher energies), where electron transfer is much less likely because the orbital overlap is less. (The interaction between the ionic and covalent configurations falls exponentially with distance.[17])

Electron transfer results from the crossing of the covalent and ionic potential energy surface, which, as suggested in Figure 2, is an avoided crossing. If neutral particles approach one another slowly, the uncertainty principle allows the energy to be well defined, and the system stays on the adiabatic surface, resulting in what we call an electron "jump". At high speeds, the system remains on the diabatic "covalent" curve, and the electron does not jump. If the ionic–covalent crossing is moved to larger distances, the ionic–covalent interaction is greatly reduced, and at a given collision energy, the likelihood of a diabatic crossing (no electron jump) is greatly increased, which mostly accounts for the lack of ions formed in the tails orientation. The higher energy of the crossing provides a rationale for the barrier to tails attack. (This description and Figure 2 are highly simplified because additional dimensions, such as the C–Br distance, must be considered to explain salt formation as well as the fragmentation observed at higher energy.)

As the energy is decreased toward thermal energy, the electron is more likely to "jump", although *the electron will jump back* if the energy is below threshold, which is likely the case for tails attack below tails threshold.[13] Salt formation (exoergic by ≈20 kcal/mol) and ion production compete with one another above the ion threshold, and it is reasonable to conclude that these processes share the same entrance channel. The preference for the Br end is thus expected to extend to lower energies, and indeed in an earlier study of K + $CF_3Br$ at thermal energies,[14] we found that the neutral salt, KBr, was more likely to be formed by Br-end attack. (A small amount of tail-end reactivity was also observed, which may be due to the quantal distribution extending into "wrong" orientations.) This picture thus suggests that these observations are likely to apply to other systems, even at lower energies, and that electron transfer is often localized.

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(12) Hasegawa, A.; Williams, F. *Chem. Phys. Lett.* **1977**, *46*, 66–68.

(13) Production of $Br^-$ by tails attack corresponds to nucleophilic substitution by the electron on the rear of the molecule via the classic Walden inversion. While overall production of $K^+$ is greater at all energies for heads attack, we are as yet unable to assess the relative importance of heads vs tails attack on the $Br^-$ channel at the onset of $Br^-$ formation.

(14) Carman, H. S.; Harland, P. W.; Brooks, P. R. *J. Phys. Chem.* **1986**, *90*, 944–948.

(15) Compton, R. N.; Reinhardt, P. W.; Cooper, C. D. *J. Chem. Phys.* **1978**, *68*, 2023–2036.

(16) Faist, M. B.; Levine, R. D. *J. Chem. Phys.* **1976**, *64*, 2953–2970.

(17) Grice, R.; Herschbach, D. R. *Mol. Phys.* **1974**, *27*, 159–175.