Communications to the Editor

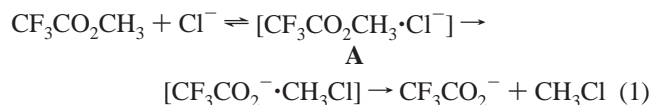## Nonstatistical Reactivity in a Vibrationally Excited S$_N$2 Intermediate

Stephen L. Craig, Meili Zhong, and John I. Brauman*

*Department of Chemistry, Stanford University
Stanford, California 94305-5080*

Received June 29, 1998

We report that the deposition of large (~55 kcal mol^{-1}) amounts of vibrational energy into an intermediate in a gas-phase S$_N$2 reaction leads to a dramatic and nonstatistical increase in the observed efficiency of the S$_N$2 substitution relative to ion−molecule dissociation. The enhanced reactivity may be attributed to the relative inefficiency of energy redistribution versus the rate of the S$_N$2 process at the energies accessed in the experiment. The behavior is different from previous reports of IVR-influenced reactivity,[1−3] in that the competing processes are quite distinct (dissociation vs reaction) and are inherently bimolecular in nature, although they proceed from a common intermediate that itself undergoes competing unimolecular processes.

The S$_N$2 reaction of Cl$^-$ + CF$_3$CO$_2$CH$_3$, eq 1, proceeds through the intermediate ion−molecule complex [CF$_3$CO$_2$CH$_3$·Cl$^-$], **A**.[4,5]

$$CF_3CO_2CH_3 + Cl^- \rightleftharpoons [CF_3CO_2CH_3 \cdot Cl^-] \rightarrow$$
$$\mathbf{A}$$
$$[CF_3CO_2^- \cdot CH_3Cl] \rightarrow CF_3CO_2^- + CH_3Cl \quad (1)$$

In this work, the intermediate **A** is generated in a vibrationally excited state (referred to hereafter as **A*****) from the carbonyl displacement reaction of CH$_3$O$^-$ + CF$_3$COCl, eq 2, which is roughly 55 kcal mol^{-1} exothermic (see Figure 1), and the reactivity of the energetic **A***** is contrasted to that observed in the less energetic intermediate of the bimolecular reaction 1.[6] As we discuss below, the observed reaction efficiency of **A***** to give the S$_N$2 product is higher than that expected from the calculated ratio of RRKM sums of states,[7−11] and the disparity between the observed reactivity and the RRKM calculations illustrates important aspects of the nature of the nonstatistical dynamics of **A** and ion−molecule S$_N$2 intermediates in general.

(1) Rynbrandt, J. D.; Rabinovitch, B. S. *J. Phys. Chem.* **1971**, *75*, 2164. Rynbrandt, J. D.; Rabinovitch, B. S. *J. Chem. Phys.* **1971**, *54*, 2275.
(2) McAdoo, D. J.; McLafferty, F. W.; Smith, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 6343. McLafferty, F. W.; McAdoo, D. J.; Smith, J. S.; Kornfeld, R. *J. Am. Chem. Soc.* **1971**, *93*, 3720. Also, see: Osterheld, T. H.; Brauman, J. I. *J. Am. Chem. Soc.* **1993**, *115*, 10311−10316.
(3) A detailed discussion of the role of IVR in unimolecular reaction dynamics may be found in: Baer, T.; Hase, W. L. *Unimolecular Reaction Dynamics: Theory and Experiments*; Oxford University Press: New York, 1996.
(4) Wilbur, J. L.; Brauman, J. I. *J. Am. Chem. Soc.* **1991**, *113*, 9699−9701.
(5) Chabinyc, M. L.; Craig, S. L.; Regan, C. K.; Brauman, J. I. *Science* **1998**, *279*, 1882−1886.
(6) Asubiojo, O. I.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 3715.
(7) Marcus, R. A. *J. Chem. Phys.* **1952**, *20*, 359.
(8) Marcus, R. A.; Hase, W. L.; Swamy, K. N. *J. Phys. Chem.* **1984**, *88*, 6717.
(9) Forst, W. *Theory of Unimolecular Reactions*; Academic Press: New York, 1973.
(10) Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions*; Blackwells Scientific: Oxford, 1990.
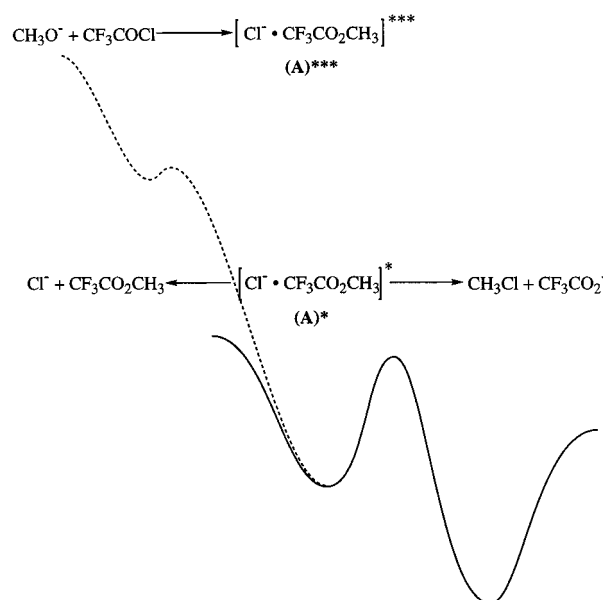(11) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Interscience: London, 1972.

Figure 1. Schematic potential energy surfaces for the generation of the activated intermediate [CF$_3$CO$_2$CH$_3$·Cl]$^-$, **A**, from the exothermic transacylation reaction of CH$_3$O$^-$ + CF$_3$COCl. Formed in this manner, **A** has a total energy approximately 55 kcal mol^{-1} above the thresholds to dissociation and S$_N$2 isomerization. The S$_N$2 barrier is within 2−3 kcal mol^{-1} of the entrance channel.

$$CH_3O^- + CF_3COCl \rightleftharpoons [CH_3O^- \cdot CF_3COCl] \rightarrow$$
$$[CF_3CO_2CH_3 \cdot Cl^-] \quad (2)$$
$$\mathbf{A^{***}}$$
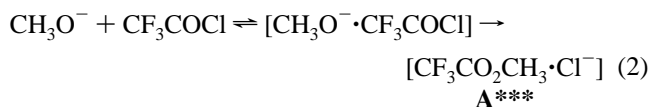
Experiments were carried out at 3×10^{-7} Torr in a FT-ICR spectrometer.[12] Methoxide ion was generated by electron impact on dimethyl peroxide; it then reacted with trifluoroacetyl chloride, yielding three ionic products: Cl$^-$, from dissociation of **A**; CF$_3$CO$_2^-$, from the S$_N$2 reaction 1; and CF$_3^-$, which may result from either a transacylation reaction of CH$_3$O$^-$ + CF$_3$COCl or decomposition of the vibrationally excited S$_N$2 product CF$_3$CO$_2^-$.[13]

The branching between these channels is summarized in Table 1. When **A** is formed from the bimolecular collision of Cl$^-$ + CF$_3$CO$_2$CH$_3$, the S$_N$2 efficiency is 0.02,[14] and an RRKM analysis shows that the observed efficiency is consistent with an energy of the transition state relative to separated reactants (ΔE_{diff}) of approximately -3 kcal mol^{-1}. Angular momentum constraints raise the effective barrier to nearly the energy of the separated reactants, and so the reaction is not expected to have a significant energy dependence.[15−17] For example, RRKM calculations in which the average internal energy of **A** is increased by 55 kcal

(12) Zhong, M.; Brauman, J. I. *J. Am. Chem. Soc.* **1996**, *118*, 636−641.
(13) It seems more likely that the CF$_3^-$ results from the S$_N$2 channel via subsequent decomposition of CF$_3$CO$_2^-$. Direct loss of CF$_3^-$ in the initial transacylation reaction is not expected to compete favorably with the much more exothermic loss of Cl$^-$.
(14) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.
(15) S$_N$2 reactions with comparable efficiencies have previously been observed to have weak temperature or internal energy dependences. See, for example, refs 16 and 17.
(16) Caldwell, G.; Magnera, T. F.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 959−966.
(17) Viggiano, A. A.; Morris, R. A. *J. Phys. Chem.* **1996**, *100*, 19227−19240.

Table 1. Products from Dissociation and S_N2 Isomerization of the Activated Intermediate $[CF_3CO_2CH_3 \cdot Cl]^-$ Generated in Two Separate Energy Regimes: from the Bimolecular Collision of $Cl^- + CF_3CO_2CH_3$ or as the Product Complex of the Exothermic Transacylation Reaction of $CH_3O^- + CF_3COCl^a$

$[Cl \cdot CF_3CO_2CH_3]^-$ source	$CF_3CO_2^-$	Cl^-	CF_3^-	fraction of S_N2^b
$Cl^- + CF_3CO_2CH_3$	0.02	0.98		0.02
$CH_3O^- + CF_3C(O)Cl$	0.07	0.85	0.08	0.08−0.15

^{a} The origin of CF_3^- in the latter case may be from either decomposition of the vibrationally excited S_N2 product $CF_3CO_2^-$ or direct transacylation by methoxide. ^{b} The fraction of $S_N2 = (S_N2$ product$)/(S_N2$ product $+ Cl^-$). If CF_3^- is an ultimate product of the S_N2 reaction the fraction of the S_N2 reaction is 0.15. If it is not, the fraction is 0.08.

mol^{-1} predict an efficiency of 0.012−0.024,[18] not significantly changed from the efficiency of the bimolecular reaction at 350 K. We observe, however, that when A^{***} is formed in that energy range from eq 2, the S_N2 efficiency is 0.08−0.15, the exact value depending on whether none or all of the CF_3^- comes from $CF_3CO_2^-$.[13] To fit the experimental minimum efficiency of 0.08, the S_N2 barrier height used in the RRKM calculations would have to be 5.5−6.5 kcal mol^{-1} below separated reactants. This value is not compatible with previous IRMPD results[4] and also the observed kinetics at 350 K,[14] both of which are consistent with a transition state that is roughly 2−3 kcal mol^{-1} below separated reactants. For example, $\Delta E_{diff} = -6$ kcal mol^{-1} corresponds to a calculated efficiency of approximately 0.14 at 350 K, well above the observed value of 0.02. Furthermore, the S_N2 efficiency of the energized A^{***} is significantly greater than that of A, suggesting that the energy of the S_N2 transition state is greater than that of the dissociated reactants ($\Delta E_{diff} > 0$),[19,20] but the absolute S_N2 efficiencies of both A and A^{***} and the IRMPD results indicate that $\Delta E_{diff} < 0$. The dynamics of the intermediate A^{***} are therefore nonstatistical in that its enhanced reactivity relative to A is not consistent with the known features of the potential energy surface.

We argue that the nonstatistical behavior of A arises because the S_N2 reaction is fast relative to the rate of energy redistribution. Recent theoretical and experimental studies of S_N2 reactions in the gas phase suggest that there is a bottleneck to energy transfer between intermolecular modes, which are active in ion−molecule association and dissociation processes, and intramolecular modes such as those required for passage through the S_N2 transition state.[21] This bottleneck has been implicated in the failure of statistical theories to describe the translational and vibrational energy dependences,[17,22,23] kinetic energy release distributions,[24] and lifetimes of the intermediates[20] of several gas-phase S_N2 reactions, including the product complex $[CH_3Cl \cdot CF_3CO_2]^-$ of eq 1.[24]

Such a bottleneck is qualitatively consistent with the results obtained in this study. If a large part of the exothermicity of the transacylation reaction 2 is initially partitioned in the intramolecular vibrational modes of A, then this energy must redistribute into intermolecular modes for dissociation to occur.[25] If redistribution is slow, then the increased energy in A^{***} would be more likely to find its way into the S_N2 reaction coordinate than expected from the calculated sum of states, leading to an S_N2 reaction efficiency that is greater than the statistical expectation. This picture of the dynamics requires that the S_N2 process be fast, and the calculated RRKM rate constant for the S_N2 unimolecular isomerization of A^{***} is approximately 5×10^{10} s^{-1}, corresponding to a time scale for reaction of around 20 ps. The rate constant is calculated by using statistical theory, and so its absolute accuracy is highly questionable. Nevertheless, it is useful to compare the calculated lifetime of A^{***} to the lifetimes of other intermediates whose dynamics have been studied previously.

For example, the lifetimes of $[Cl \cdot CH_3Cl]^-$ (and, by analogy, $[Cl \cdot CH_3Br]^-$) are also on the order of tens of picoseconds,[20] and energy does not redistribute efficiently in these S_N2 intermediates, either.[22,26] By comparison, the translational energy dependencies of a series of S_N2 and carbonyl addition−elimination (AE) rate constants have been studied recently, and the observed energy dependencies are consistent with RRKM calculations, suggesting that T $\leftrightarrow$ V energy redistribution is efficient in those reactant complexes.[27−29] The calculated intermediate lifetimes of the reactions that behave statistically, however, are 10 ns or longer.[27−29] The efficiency of energy transfer has been observed previously to correlate with the expected lifetime of the intermediate.[30] For the intermediates of S_N2 and related reactions, lifetimes of tens of picoseconds are not sufficiently long for energy to redistribute statistically, while lifetimes on the order of 10 ns or longer appear to be sufficient. The nonstatistical dynamics of A^{***}, then, are not surprising given its expected short lifetime for S_N2 reactivity. The study of reactive intermediates with lifetimes in the subnanosecond range should continue to yield a wealth of insight into the dynamics of S_N2 and other ion−molecule reactions.

(18) The exact statistical expectation depends slightly on the angular momentum distribution of the reactants that cross the transacylation transition state. The range presented in the text represents the efficiencies calculated from a wide range of possible distributions.

(19) Magnera, T. F.; Kebarle, P. In *Ionic Processes in the Gas Phase*; Almoster Ferreira, M. A., Ed.; D. Reidel Publishing Co.: Dordrecht, 1984; Vol. 118, p 135.

(20) Li, C.; Ross, P.; Szulejko, J. E.; McMahon, T. B. *J. Am. Chem. Soc.* **1996**, *118*, 9360−9367.

(21) Hase, W. L. *Science* **1994**, *266*, 998−1002.

(22) Viggiano, A. A.; Morris, R. A.; Paschkewitz, J. S.; Paulson, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 10477.

(23) Wang, H.; Peslherbe, G. H.; Hase, W. L. *J. Am. Chem. Soc.* **1994**, *116*, 9644. Wang, H.; Hase, W. L. *J. Am. Chem. Soc.* **1995**, *117*, 9347−9356. Wang, H.; Hase, W. L. *Chem. Phys.* **1996**, *212*, 247−258. Wang, H.; Goldfield, E. M.; Hase, W. L. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 737−746.

(24) Graul, S. T.; Bowers, M. T. *J. Am. Chem. Soc.* **1991**, *113*, 9696−9697. Graul, S. T.; Bowers, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 3875. Graul, S. T.; Carpenter, C. J.; Bushnell, J. E.; van Koppen, P. A. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1998**, *120*, 6785−6796.

(25) The kinetic energy release distributions measured for S_N2 reactions by Graul and Bowers, ref 24, demonstrate that, for those reactions, the exothermicity is initially partitioned in product vibrational, rather than relative translational, degrees of freedom.

(26) Vande Linde, S. R.; Hase, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 2349−2351. Vande Linde, S. R.; Hase, W. L. *J. Phys. Chem.* **1990**, *94*, 6148−6150. Vande Linde, S. R.; Hase, W. L. *J. Phys. Chem.* **1990**, *94*, 2778−2788. Vande Linde, S. R.; Hase, W. L. *J. Chem. Phys.* **1990**, *93*, 7962.

(27) Viggiano, A. A.; Morris, R. A.; Su, T.; Wladkowski, B. D.; Craig, S. L.; Zhong, M.; Brauman, J. I. *J. Am. Chem. Soc.* **1994**, *116*, 2213−2214.

(28) Craig, S. L.; Brauman, J. I. *Science* **1997**, *276*, 1536−1538.

(29) Craig, S. L.; Brauman, J. I. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 510−515. Craig, S. L.; Zhong, M.; Brauman, J. I. In preparation.

(30) Boering, K. A.; Brauman, J. I. *J. Chem. Phys.* **1992**, *97*, 5439.