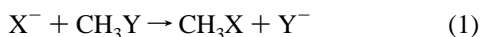## Photoinitiation of Gas-Phase S_N2 Reactions through the Evans−Polanyi Excited State Surface

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In the classic Evans-Polanyi treatment[1,2] of the S_N2 reaction

$$X^- + CH_3Y \rightarrow CH_3X + Y^- \qquad (1)$$

the Walden inversion transition state[3] is recovered *via* an avoided crossing between diabatic curves that arise from the hypothetical transfer of the methyl group without concomitant electron transfer. These curves are sketched in Figure 1 for the reaction $I^- + CH_3NO_2$.[4] The matrix element splitting these curves is related to the electron transfer rate (*i.e.*, resonance energy) at the transition state (~ 0.5 eV).[2] The avoided crossing results in a low-lying electronically excited charge transfer (CT) state correlating to $I \cdot [CH_3NO_2]^-$ and $[CH_3I]^- \cdot NO_2$ over the geometries of the (gas phase) ion−dipole minima. The excited state has a deep minimum in the transition state region of the S_N2 reaction and should therefore provide a unique platform for carrying out direct spectroscopic observations of the transition state below. We have reported[5] several attempts to access these excited states by photoexcitation of ion−dipole complexes and have found that while they were not directly accessed from the ground state, they could be reached *indirectly* through the diffuse, dipole-bound excited state lying just below the electron continuum.[6] In the best studied case of $I^- \cdot CH_3I$,[5] however, indirect excitation of the CT state failed to drive the S_N2 reaction, presumably due to the very repulsive nature of CH_3I^- which leads to prompt dissociation along the $[ICH_3I]^-$ antisymmetric stretch coordinate (*i.e.*, to $I^- + CH_3 + I$).

In this paper, we report the successful initiation of the reactions[4]

$$X^- + CH_3NO_2 \rightarrow NO_2^- + CH_3X \quad (X = I, Br, Cl) \quad (2)$$
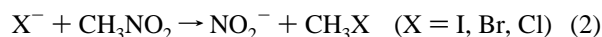
by photoexcitation of the stabilized $X^- \cdot CH_3NO_2$ reaction intermediates to the $X \cdot [CH_3NO_2]^-$ charge transfer excited states. Unlike the CH_3Y^- anions created upon photoexcitation of the $X^- \cdot CH_3Y$ (Y = halogen) complexes, the $CH_3NO_2^-$ ion is bound $[D_0(CH_3-NO_2^-) = 0.56$ eV][7] and its stability enables the charge transfer excited state to remain intact, leading to products consistent with reaction on the ground state surface. This work constitutes the first spectroscopic observation of this classic Evans−Polanyi excited state surface.

(1) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1938**, *34*, 11. Ogg, R. A.; Polanyi, M. *Trans. Faraday Soc.* **1935**, *31*, 604.

(2) Shaik, S. S.; Schlegel, H. B.; Wolfe, S. *Theoretical Aspects of Physical Organic Chemistry: The S_N2 Mechanism*; Wiley-Interscience: New York, 1992.

(3) (a) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219. (b) Graul, S. T.; Bowers, M. T. *J. Am. Chem. Soc.* **1991**, *113*, 9696. (c) DePuy, C. H.; Gronert, S.; Mullin, A.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1990**, *112*, 865. (d) Viggiano, A. A.; Morris, R. A.; Pashkewitz, J. S.; Paulson, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 10477.

(4) Tanaka, K.; McKay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643.

(5) (a) Cyr, D. M.; Bishea, G. A.; Scarton, M. G.; Johnson, M. A. *J. Chem. Phys.* **1992**, *97*, 5911. (b) Cyr, D. M.; Bailey, C. G.; Serxner, D.; Scarton, M. G.; Johnson, M. A. *J. Chem. Phys.* **1994**, *101*, 10507.

(6) Dessent, C. E. H.; Bailey, C. G.; Johnson, M. A. *J. Chem. Phys.* **1995**, *102*, 6335. Dessent, C. E. H.; Bailey, C. G.; Johnson, M. A. *J. Chem. Phys.* **1995**, *103*, 2006.

(7) Compton, R. N.; Carman, H. S.; Desfrancois, C.; Abdoul-Carime, H.; Schermann, J. P.; Hendricks, J.; Lyapustina, S. A.; Bowen, K. H. *J. Chem. Phys.* **1996**, *105*, 3472.
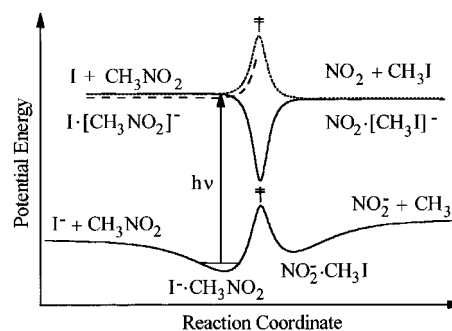
Figure 1. Schematic potential energy surface of the gas phase S_N2 reaction $I^- + CH_3NO_2 \rightarrow NO_2^- + CH_3I$ along the reaction coordinate. The surface for the corresponding neutral reaction is shown at the top of the diagram, with its associated dipole-bound anionic excited state (dashed line).

We carry out these experiments using a tandem time-of-flight mass spectrometer,[8] where the $X^- \cdot CH_3NO_2$ complexes are generated in a free jet expansion by association onto X^- ions created by secondary electron attachment to CCl_4, CH_2Br_2, or CH_3I (for Cl^-, Br^-, and I^-, respectively). The nitromethane (40 Torr) was seeded along with the halide precursors in 4 atm of Ar. The UV bands of the complexes were scanned using the frequency-doubled or sum frequency mixed (with 1.165 eV) signal beam from a β-barium borate (BBO) optical parametric oscillator (Spectra Physics MOPO-710). Fragment ions were separated using a reflectron, and action spectra for particular photoproducts were obtained by selectively detecting a fragment ion with a boxcar averager while the laser was scanned.

The charge transfer excited states, $X \cdot [CH_3NO_2]^-$, are expected to lie close to the vertical detachment energies (VDE) of these complexes since the vertical electron affinity of CH_3NO_2 is approximately 0.[7] The $I^- \cdot CH_3NO_2$ photoelectron spectrum displayed very little vibrational fine structure, consistent with the other $I^- \cdot CH_3Y$ (Y = CN, I, Br) complexes we have studied,[5,6] where the ion is calculated to sit in the "pocket" behind the methyl group. The location of the band was first established by monitoring the fast "photoneutrals" which accompany photodestruction of the parent ion. A strong band appeared just below the VDE (3.604 ± 0.01 eV for $I^- \cdot CH_3NO_2$, recall that the electron affinity of the iodine atom is 3.06 eV) with the characteristic shape for excitation of a dipole-bound excited state.[6] Such a band is expected since the dipole moment of CH_3NO_2 (3.46 D) is much larger than the critical value required to support a bound state ($\mu_{crit} \approx 2-2.5$ D).

A mass spectrum of the ionic photofragments produced at the peak of the $I^- \cdot CH_3NO_2$ absorption is presented in Figure 2a, showing not only the expected $CH_3NO_2^-$ anion but also the I^- and NO_2^- anions. Figure 3 displays the action spectrum for production of the NO_2^- photofragment, illustrating that the band is sharply peaked just below the VDE of the complex (arrow in Figure 3) in the region where a dipole-bound state is expected to occur. This indicates that the NO_2^- fragmentation channel is enhanced through the dipole-bound excited state of $I^- \cdot CH_3NO_2$ (the I^- action spectrum tracks the NO_2^- channel). A small progression is observed above the VDE; similar features were observed and analyzed[9] in the $I^- \cdot CH_3I$ system in the context of vibrational excitation arising from nonadiabatic coupling between the free electron and CH_3I. In the present case, the 79 ± 3 meV spacing of the features in Figure 3 roughly corresponds to either the NO_2 bending or wagging mode in

(8) Johnson, M. A.; Lineberger, W. C. *Techniques in Chemistry*; Farrar, J. M., Saunders, W. H., Eds.; Wiley: New York, 1988; p 591.

(9) Dessent, C. E. H.; Bailey, C. G.; Johnson, M. A. *J. Chem. Phys.* **1996**, *105*, 10416.
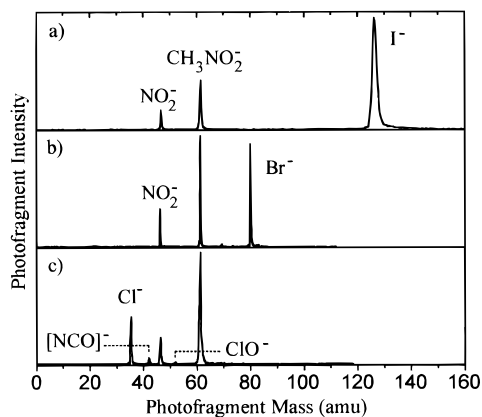
Figure 2. Ionic photofragment mass spectra from excitation of (a) $I^-\cdot CH_3NO_2$ at 3.54 eV, (b) $Br^-\cdot CH_3NO_2$ at 3.96 eV, and (c) $Cl^-\cdot CH_3NO_2$ at 4.29 eV.
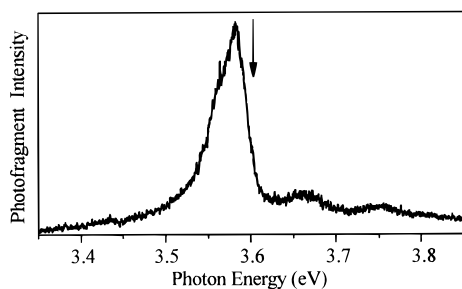

Figure 3. NO_2^- photofragment action spectra from $I^-\cdot CH_3NO_2$, plotted *vs* laser excitation energy. The arrow represents the VDE of $I^-\cdot CH_3NO_2$.
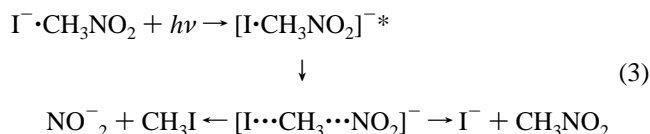
neutral CH_3NO_2 (81 and 75 meV, respectively),[10] as would be expected for scattering through a $CH_3-NO_2^-$ transient negative ion.

The NO_2^- and I^- fragments were unexpected, since we have not previously observed I^- production from excitation of $I^-\cdot M$ dipole-bound excited states, (*cf* $I^-\cdot CH_3CN + h\nu \rightarrow CH_3CN^- + I$).[6,11] Another complication arising in this system is that the $CH_3NO_2^-$ anion is known to occur in two forms which are separated by a barrier: a dipole-bound form with a diffuse electron and the covalent anion where the excess electron penetrates into the molecular orbitals and causes strong distortion along the $C-NO_2$ wag.[7] We have determined that the $CH_3NO_2^-$ anion observed in this experiment (Figure 2a) is readily field-detached (≈ 12 kV/cm), indicating that the dipole-bound form is the dominant photoproduct. At the detachment threshold, this nascent $CH_3NO_2^-$ ion is stable relative to dissociative attachment to form NO_2^- (by 0.56 eV) so that *production of the NO_2^- ion requires (on energetic grounds) that the dipole-bound excited state $[I\cdot CH_3NO_2]^-*$ decays with the formation of a CH_3-I bond.* Formation of the $C-I$ bond, in turn, requires crossing back to the ground state surface (see Figure 1), since the excited state correlates to $CH_3 + I^-$ which is repulsive. Thus,

(10) Grose. D.; Cavagnat, D.; Pesquer, M.; Lapouge, *J. Phys. Chem.* **1993**, *97*, 4262.

(11) The $I^-\cdot CH_3I$ system is a special case since electron attachment to methyl iodide initiates dissociative attachment, thereby producing an I^- photofragment.[5]

photoexcitation of the $I^-\cdot CH_3NO_2$ complex leads to the ions expected for decomposition on the ground state, S_N2 surface:

$$I^-\cdot CH_3NO_2 + h\nu \rightarrow [I\cdot CH_3NO_2]^-*$$
$$\downarrow \qquad\qquad\qquad (3)$$
$$NO_2^- + CH_3I \leftarrow [I\cdots CH_3\cdots NO_2]^- \rightarrow I^- + CH_3NO_2$$

with an I^-/NO_2^- branching ratio (25:1 for the peak areas)[12] favoring the exothermic I^- direction ($\Delta E = +0.8$ eV for reaction 2).[13]

A relatively simple check on whether the I^-/NO_2^- branching ratio indeed reflects partitioning on the ground state surface can be obtained by chemically derivatizing the system. The exothermicity of reaction 2 decreases for the lighter halogens (0.80, 0.50, and 0.15 eV for I^-, Br^- and Cl^-, respectively)[13] suggesting that the X^-/NO_2^- branching ratio should become smaller along the I/Br/Cl series. The $Br^-\cdot CH_3NO_2$ and $Cl^-\cdot CH_3NO_2$ complexes again display strong absorptions arising from dipole-bound states in the vicinities of their VDEs, and the fragment ion mass spectra arising from excitation close to the absorption maxima are displayed in Figure 2b,c. Both Cl^- and Br^- systems again photodissociate into NO_2^- and X^- in addition to $CH_3NO_2^-$. The fragment mass spectra illustrate that the X^-/NO_2^- branching ratios (25:1, 3:1, and 1.4:1 for the I^-, Br^-, and Cl^- complexes) indeed decrease as reaction 2 becomes less exothermic. Crude RRKM calculations indicate that the observed branching ratios are in the range anticipated[16] for decomposition on the ground state surface. While more detailed investigations will be necessary to fully characterize the ground state geometry and excited state dynamics, the ability to access the charge transfer state, and hence the deep minimum that lies above the S_N2 transition state, is a significant experimental advance as it provides a unique spectroscopic route for studying the transition state. For example, by beginning the experiment with a solvated complex such as $I^-\cdot CH_3NO_2\cdot Ar_n$, it might be possible to quench the complex in the excited state minimum through evaporative cooling by the spectator argon atoms.

(12) The X^-/NO_2^- fragment ratios should be corrected to account for the mass dependent detection efficiency at constant velocity in the reflectron. We measured the detection efficiency of I^- compared to O_2^- when both ions have the same velocity (I^- KE = 4.5 keV) by ratioing the depleted ion signal to the number of photoelectrons ejected. I^- was detected $\sim 30\%$ more efficiently than O_2^-, so that a correction on this order must be applied; however, this effect is much smaller than the observed differences in branching ratios so that the general trend is intact.

(13) $\Delta E = EA(NO_2) + D_0(CH_3-X) - EA(X) - D_0(CH_3-NO_2)$.[14,15]

(14) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Homes, J. L.; Levin, R. D.; Mallard, W. D. *J. Phys. Chem. Ref. Data* **1988**, *117*, Supplement No. 1.

(15) *CRC Handbook of Chemistry and Physics*, 77th ed.; CRC Press: Boca Raton, FL, 1996.

(16) Branching from a single transition state ($[X\cdots CH_3\cdots NO_2]^-$) was considered by estimating frequencies[3a] and then averaging to give one frequency group. The branching ratios obtained were 26:1, 6:1, and 1.7:1 for I^-/NO_2^-, Br^-/NO_2^-, and Cl^-/NO_2^- respectively. Secondly, we considered branching from two "product-like" transition states for each system, again averaging frequencies into one frequency group. This procedure gave the ratios as 13:1, 3:1, and 1:1. We emphasize that while these calculations oversimplify the problem, they suggest that the experimental ratios are of the magnitude expected for branching on the ground state surface.