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Dissociative Attachment as a Probe of Intramolecular Electron Transfer

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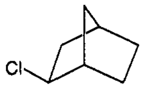
Low-energy electron-scattering processes are sensitive to the interaction of distant functional groups in chromophore–bridge–chromophore molecules through the formation of temporary anion states created by the occupation of normally unfilled molecular orbitals.[1] Here we show that the dissociative attachment (DA) process,

$$e^- + XY \rightarrow XY^{-*} \rightarrow X + Y^-$$

one of the possible decay channels of a temporary anion state, provides a useful probe of long-range intramolecular interactions and electron transfer. Two unique aspects of this study are that the measurements are made in the gas phase and that the initially prepared anion states have very short lifetimes, typically 10^{-14}–10^{-15} s. Specifically, we report measurements of the DA cross sections of *exo*-2-chloronorbornane (**1**), *exo*-5-chloro-2-norbornene (**2**), and *syn*-7-chloro-2-norbornene (**3**) and show that the yield of Cl^- is a factor of 71 greater in **2** than in **1** due to the coupling between the localized C—Cl σ^* and C═C π^* orbitals. Such an enhancement in the Cl^- production is not observed for **3** which π^*/σ^* coupling is symmetry forbidden because the Cl atom lies in the nodal plane of the π^* orbital. The details of the DA apparatus and experimental procedure will be reported elsewhere.[2]



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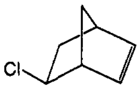

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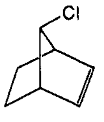

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The DA process is initiated by capture of an impinging electron into a normally unoccupied molecular orbital of the neutral molecule. A temporary anion is thus formed whose lifetime, given by the time required for the electron to tunnel back into the continuum, depends on the electron's energy as well as the shape and nodal characteristics of the orbital.[3] If the temporarily occupied orbital has a component that is C–Cl antibonding (*i.e.*, σ^*), the anion may decay by production of Cl^-.

Figure 1a shows the total DA cross section for the saturated compound **1** as a function of the electron impact energy. The cross section peaks[4] at 1.65 eV and has a magnitude of 6.9×10^{-19} cm^2 ± 20%. The data shown in Figure 1a are typical of monochloroalkanes which contain two or more carbon atoms. For example, the cross section for **1** is intermediate in magnitude between those for *n*-chloropropane and 2-chloropropane.[2] In the saturated monochloroalkanes, the DA process takes place through electron capture into the lowest-lying σ^* orbital, which is localized primarily on the C–Cl bond. The peak in the DA cross section of **1** lies 0.65 eV lower in energy than the peak in the electron attachment cross section,[1b] determined by means of electron transmission spectroscopy (ETS).[5] This shift is well understood[6] and occurs because the autodetachment rate of the electron from the temporary anion is large in the vertical attachment region and decreases rapidly with increasing C–Cl bond length. Temporary anions formed in the vertical attachment region are therefore less likely to survive to produce Cl^- than those formed at larger C–Cl distances. In general, as the lifetime of the anion becomes shorter, the shift becomes larger.

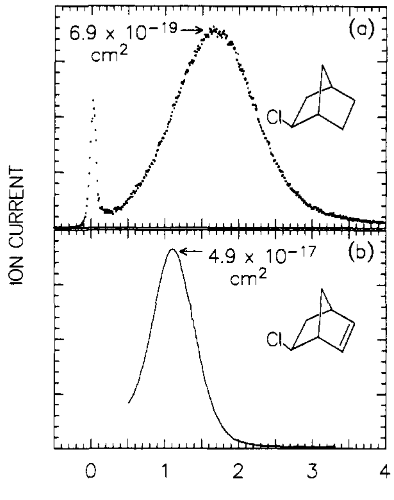

Figure 1. Dissociative attachment cross sections of (a) *exo*-2-chloronorbornane (**1**) and (b) *exo*-5-chloro-2-norbornene (**2**) as a function of electron impact energy.

The DA cross section of **2** is shown in Figure 1b. The maximum in the cross section is 4.9×10^{-17} cm^2 ± 20%, which is 71 times larger than that determined for **1**. Furthermore, the peak in the DA cross section lies at 1.1 eV, substantially lower in energy than that for **1**. ETS measurements show[1b] that temporary anion states in **2** lie at 1.10 and 2.78 eV. The lower energy anion state is due to electron capture into the C═C π^* orbital and the upper state to capture into the C—Cl σ^* orbital. The DA peak therefore appears precisely at the energy of the π^* anion state, and, moreover, it has nearly the same width as the peak due to the π^* anion state in the electron transmission spectrum. These data provide compelling evidence that the Cl^- production in **2** results from electron capture into the π^* orbital. Theoretical calculations[7] indicate that there is both through-bond[8] and through-space coupling between the π^* and σ^* orbitals of **2**. It is this coupling which leads to the production of Cl^- at the energy of the π^* anion state.

The DA cross section of **3** (not shown) is even smaller than that of **1**, and only an estimate of 2×10^{-20} cm^2 could be obtained. The maximum occurs at an energy of 1.1 eV. As noted earlier, direct coupling between the π^* and σ^* anion states in this molecule

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[1] (a) Balaji, V.; Jordan, K. D.; Burrow, P. D.; Paddon-Row, M. N.; Patney, H. K. *J. Am. Chem. Soc.* **1982**, *104*, 6849. Balaji, V.; Ng, L.; Patney, H. K.; Jordan, K. D.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1987**, *109*, 6957. (b) Morrison, H. A.; Singh, T. V.; de Cardenas, L.; Severance, D.; Jordan, K. D.; Schaefer, W. *J. Am. Chem. Soc.* **1986**, *108*, 3862. (c) Maxwell, B. D.; Nash, J. J.; Morrison, H.; Falcetta, M. F.; Jordan, K. D. *J. Am. Chem. Soc.* **1989**, *111*, 7914.

[2] Pearl, D. M.; Burrow, P. D., manuscript in preparation.

[3] Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341.

[4] The narrow peak at zero energy may be due to a trace amount of CCl_4.

[5] Sanche, L.; Schulz, G. J. *Phys. Rev. A* **1972**, *5*, 1672.

[6] O'Malley, T. F. *Phys. Rev.* **1967**, *155*, 59.

[7] Nash, J. J.; Jordan, K. D., unpublished results.

[8] Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499.

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is symmetry forbidden. Our ETS measurements locate the π^* and σ^* anion states at 1.25 and 2.75 eV, respectively. We believe that the lifetime of the upper state, which lies about 0.35 eV *higher* than those in the *n*-chloroalkanes, is so short that direct electron capture into the C–Cl σ^* orbital does not yield measurable Cl^- [9] and that the small Cl^- signal may derive from vibronic mixing between the two anion states.

Potential energy curves describing the DA process in **2** in both diabatic and adiabatic representations are shown schematically in Figure 2.[10] The reaction coordinate is labeled as the C–Cl bond length, although other degrees of freedom are involved. In the diabatic representation, the σ^* anion state of **2** lies about 1.1 eV above the π^* anion state in the vertical attachment region. The energy of the σ^* anion state decreases rapidly with increasing C–Cl bond length, while that of the π^* anion state increases. As a result, the diabatic potentials cross at a C–Cl bond length somewhat greater than the equilibrium value in the ground state. As mentioned above, vertical electron capture into the σ^* orbital does not lead to appreciable Cl^- formation due to the short anion lifetime. However, the anion formed by electron capture into the π^* orbital has a much longer lifetime,[11] enabling a significant fraction of the anions to reach the crossing region and to "jump" onto the dissociative σ^* surface. This takes place on a portion of the σ^* surface where the lifetime is longer than in the vertical attachment region. In an adiabatic picture, there is an avoided crossing between the two anion states, and the splitting between the two states gives the coupling responsible for the electron transfer from the π^* moiety to the C–Cl σ^* acceptor group.[12]

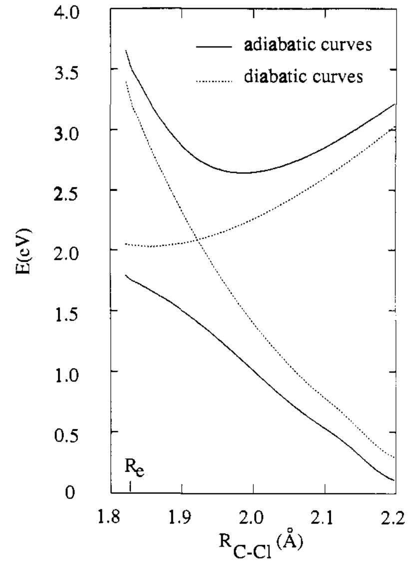

Figure 2. Potential energy curves for the π^* and σ^* anion states of *exo*-5-chloro-2-norbornene (**2**) in both the adiabatic (solid curves) and diabatic (dashed curves) representations as a function of the C–Cl bond length (from ref 10). The equilibrium bond length of the neutral molecule is denoted by R_e. At C–Cl distances shorter than the crossing point between the diabatic curves, the π^* anion lies lower in energy, and at larger distances the σ^* anion is lower in energy.

The present study demonstrates that the dissociative attachment process can be used as a sensitive probe of the electronic coupling between distant functional groups in gas-phase molecules. Future studies will address the dependence of the Cl^- yield on the lifetime of the π^* anion state and on the length of the bridge separating the π^* and C–Cl σ^* groups.

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[9] Model calculations by I. I. Fabrikant (personal communication) suggest that the magnitude of the DA cross sections for Cl^- production in alkyl chlorides decreases rapidly with increasing vertical attachment energy.

[10] Nachtigallova, D.; Jordan, K. D., unpublished results.

[11] Electron autodetachment is slower from the π^* anion state than from the σ^* anion state due to the higher potential barrier surrounding the C=C group.

[12] Strictly speaking, this statement pertains only to the weak coupling limit. Although the π^*/σ^* coupling in **2** is too large for this limit to be applicable, it can be attained by increasing the length of the bridge separating the ethylenic and C–Cl groups.