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An Unusual Zwitterionic, Diradical Intermediate in Photochemical Electron-Transfer Substitution Reactions

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A novel mode of reactivity between Lewis bases and alkyl halides was recently described in solution[1] and on diamond surfaces,[2] wherein the halogen atom was replaced by the heteroatom of the Lewis base via an unusual photoinduced substitution reaction, shown in Scheme 1. In this reaction mechanism, an equilibrium charge-transfer (donor−acceptor) complex intermediate **1** is formed, by overlap of the lone pair of a Lewis base donor (amine, alcohol, or thiol) with the carbon−halogen (R−X) σ^* orbital acceptor. Irradiation at the charge-transfer band present in the ultraviolet[3] apparently induced electron transfer from an amine to the alkyl halide, resulting in loss of the halide ion through a process equivalent to dissociative electron attachment.[4,5] This was followed by rearrangement to form the alkyl-substituted base and hydrogen halide. Inhibition experiments showed that free radicals were not involved in the substitution reaction pathway.[1] Instead, the unusual intermediate **2**, formally a zwitterion diradical, was proposed. In this communication, we report the direct observation of **2** by electron spin resonance (ESR) spectroscopy. We also present density functional calculations of the physical and spin-electronic structures of **1** and **2**.

ESR spectra were obtained using a JEOL JES-TE100 spectrometer operating at 9.2 GHz and equipped with a liquid helium-cooled, variable-temperature cryostat and included a quartz window to permit in situ ultraviolet irradiation of the sample. The output of a 1000 W Xe arc lamp was filtered (10 nm band-pass) by a 0.125-m grating monochromator and focused onto the sample. Samples were degassed before use.[6]

No ESR signal could be discerned for the liquid solution of 1-chloroadamantane and *tert*-butylamine, regardless of illumination wavelength. Unirradiated samples also had no ESR signal. In irradiated solid solution, long-lived species with unpaired spins and lifetimes of hours could be observed. Upon remelting, the ESR signal disappeared within seconds. The same sample could be used for numerous irradiations by allowing it to melt, then refreeze in the dark. A small amount of precipitate (a mixture of *tert*-butylammonium chloride and *N*,*N*-tert-butyl-1-adamantylammonium chloride)[1] could be observed in the thawed sample tube after illumination near the charge-transfer band, but this did not affect the qualitative observations.

Figure 1 shows the first-derivative X-band electron spin resonance spectrum[7] of the photoinduced charge-transfer complex intermediate **2** during irradiation at 25 K of the 1:1 mixture at 255 nm, near the 258-nm λ_{max} of the donor−acceptor charge-transfer complex **2**.[3] This assignment was made on the basis of the correlation of the maximum intensity of this characteristic signal with the reported maximum in the substitution-photoreactivity action spectrum.[1]

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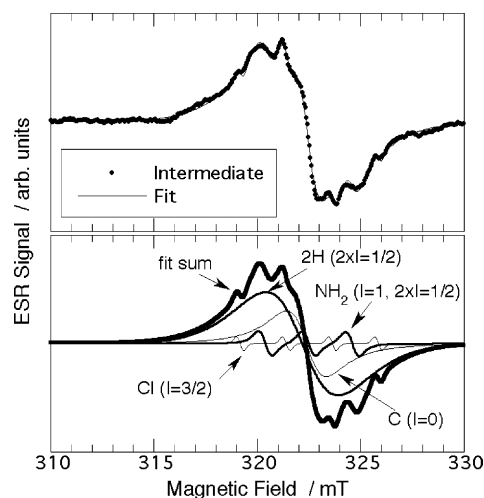
Figure 1. (Top) First-derivative X-band electron spin resonance spectrum of the photoinduced charge-transfer complex **2** at 25 K. The points are the experimental data; the line is a fit to the data. (Bottom) Deconvoluted components of the fitted spectrum.

Scheme 1. Photoinduced Electron-Transfer Substitution Reaction between an Alkyl Halide and a Lewis Base (B) via a Charge-Transfer Intermediate
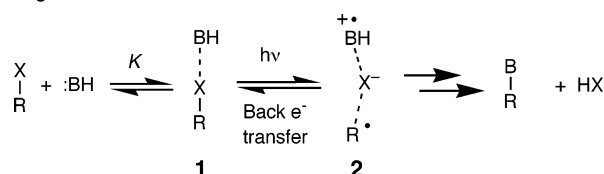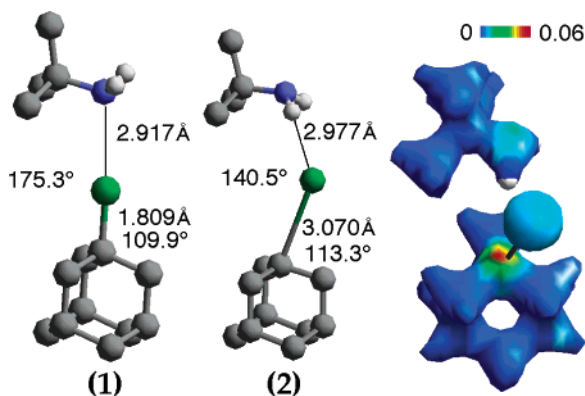

The approximately isotropic spectrum of this intermediate clearly has several hyperfine spin components. The 1:1:1:1 chlorine quadruplet ($I = 3/2$ for ^{35}Cl and ^{37}Cl, $g = 2.0042$, $A = 2.232$ mT) and the 1:1:1 nitrogen triplet ($I = 1$ for ^{14}N, $g = 2.00043$, $A = 2.097$ mT with unresolved superhyperfine coupling of ca. 0.22 mT to the amine ^{1}H) are apparent.[8] A ^{12}C-coupled singlet ($I = 0$, $g = 2.0051$) and a broad, unresolved 1:2:1 triplet, resulting from coupling to the two amine hydrogens ($I = 1/2$, $g = 2.0063$, $A = 0.018$ mT), were required to account for the remaining spectral curvature and intensity distribution. We did not observe a $\Delta M_S = 2$ triplet signal near half-field.[9] Presumably this is due to weak exchange between the N-centered and C-centered radicals.[10] Mechanisms for diradical exchange include through-space and through-bond coupling. The former is likely to be limited in this system given the long C−N distance (5.691 Å, vide infra). The latter is also negligible, since there is no C−N orbital overlap and the C−Cl bond has been broken.

When the mixture was irradiated at wavelengths significantly shorter than the λ_{max} of complex **1** (e.g., 210 nm), the spin resonance signal of the mixture was essentially identical to that of the pure

Figure 2. Calculated structures for the ground-state charge-transfer complex **1** and the photogenerated zwitterionic diradical intermediate **2**. (C-dark gray, N-blue, H-light gray, Cl-green; non-amine hydrogens have been omitted for clarity.). The dimensions shown refer to the N−Cl and Cl−C bond lengths and the N−Cl−C and bridgehead C−C−C bond angles. Also shown is the calculated false-color spin-density map of **2** superimposed on its total electron density isosurface. The contour-plot structure has been tilted to better show the amine.

alkyl halide irradiated at that wavelength, indicating that carbon−halogen bond homolysis was the primary photoprocess, consistent with the previously observed product distribution.[1] The species observed were the adamantyl radical ($g = 2.0051$)[11] and the $^2P_{3/2}$ chlorine radical ($g = 2.0239$, $A = 0.0002$ mT). This appears to be the first report of successful measurement of a condensed-phase $^2P_{3/2}$ Cl ESR signal.[12−14] Unsurprisingly, when the mixture was irradiated at wavelengths significantly longer than λ_{max} (e.g., 300 nm), no spin resonance signal was observed.[3]

To probe this system further, we performed a density functional study.[15] The calculated structures for the charge-transfer complex **1** and the photogenerated intermediate **2** are shown in Figure 2. The intermediate **2** was generated from the structure of complex **1** by setting the spin state to a triplet and allowing the structure to relax. When the spin state of **2** was set to a singlet, its structure reverted to **1**, suggesting that these calculated structures are part of a single reactivity manifold, related by an intersystem crossing. The adamantyl moiety of **2** showed significant planarization of the tertiary radical carbon, while the C−Cl distance increased. The N−Cl−C angle is bent, suggestive of a precursor state for N−C bond formation in the final steps of Scheme 1. The amine moiety in **2** was inverted relative to the complex **1**, probably because of the negative charge density on the chloride.

The calculated spin density of the intermediate **2** is shown in Figure 2 as a false-color map superimposed on a total electron density isosurface of the complex. On the carbon radical, the spin density was high and localized. The spin density on the amine was lower and more diffuse. There is also nonzero spin density on the chlorine. Thus, we can account for the obvious N, C, and Cl contributions to the spin Hamiltonian.

To understand the hydrogen hyperfine coupling, it is useful to consider the composition of the relevant molecular orbitals. A density of states analysis revealed that the N-based singly occupied molecular orbital (SOMO) is fundamentally a N(2p, $m_l = 0$) orbital with minor density contributions from the N(2s) and the other two N(2p) components. The ^1H superhyperfine coupling to the SOMO is therefore weak because the Fermi contact is primarily transmitted through s-orbital components that have appreciable nuclear penetration. The ^1H hyperfine coupling by the two amine hydrogens likely originates from spin-transfer to the orthogonal H(1s)-containing bonding orbitals of the NH$_2$ functionality; these are composed of N(2s) and N(2p, $m_l = \pm1$) but negligible N(2p, $m_l = 0$).

The direct observation of intermediate **2** provides experimental verification of the photoinduced electron-transfer substitution reaction given in Scheme 1. Similar photosubstitutions have been carried out for a range of Lewis bases, including other amines, alcohols, and thiols.[1,2] On the basis of the measured action spectra, they appear to proceed as shown in Scheme 1 and involve intermediates analogous to **2**.

Supporting Information Available: Cartesian coordinates for structures **1** and **2** (plain text). Additional ESR spectra and frontier molecular orbital isosurfaces (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Miller, J. B.; Salvador, J. R. *J. Org. Chem.* **2002**, *67*, 435.
(2) Miller, J. B. *Surf. Sci.* **1999**, *439*, 21.
(3) Miller, J. B.; Kondilenko, V. P.; Salvador, J. R.; Pontes, R. *Spectrochim. Acta, Part A* **2003**, *59*, 777.
(4) Smith, D.; Herd, C. R.; Adams, N. G. *Int. J. Mass Spectrom. Ion Processes* **1989**, *93*, 15.
(5) Matchkarovskaya, I. A.; Burshtein, K. Ya.; Faustov, V. I. *J. Mol. Struct. (THEOCHEM)* **1995**, *338*, 101.
(6) *tert*-Butylamine was always freshly distilled, and 1-chloroadamantane was first vacuum-sublimed (ca. 10^{-1} Torr, 40−45 °C) and then recrystallized from hot ethanol prior to use when necessary. Sample solutions were 1 mol L^{-1} 1:1 methylcyclopentane/methylcyclohexane solutions of either *tert*-butylamine, 1-chloroadamantane, or a 1:1 mixture of the two.
(7) ESR signals due to uncomplexed donor amine and acceptor halide have been spectrally subtracted using peripheral features to empirically determine scaling. Reported spin-Hamiltonian parameters were determined by least-squares fitting of simulated spectra that incorporated hyperfine and superhyperfine components but no perturbation theory.
(8) Hyperfine couplings of this magnitude have been observed for α-^1H in benzosemiquinone radical anions. See: Sinnecker, S.; Reijerse, E.; Neese, F.; Lubitz, W. *J. Am. Chem. Soc.* **2004**, *126*, 3280.
(9) Such signals have been used to confirm certain diradicals. For example, see: Sheila, I.; Hauck, S. I.; Lakshmi, K. V.; Hartwig, J. F. *Org. Lett.* **1999**, *1*, 2057.
(10) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance: Elementary Theory and Practical Applications*; Chapman and Hall: New York, 1986; pp 250−251.
(11) Mishra, S. P.; Symons, M. C. R. *Tetrahedron Lett.* **1973**, 2267.
(12) Jen, C. K.; Foner, S. N.; Cochran, E. L.; Bowers, V. A. *Phys. Rev.* **1958**, *112*, 1169.
(13) Trofimov, V. I.; Buben, N. Ya. *Dokl. Akad. Nauk SSSR* **1970**, *193*, 645.
(14) The gas-phase spectrum of Cl• has been reported. See: Beltran-Lopez, V.; Robinson, H. G. *Phys. Rev.* **1961**, *123*, 161.
(15) DMol^3 (Delley, B. *J. Chem. Phys.* **1990**, *92*, 508) as implemented in Accelrys' Cerius^2. Local-density PWC functionals (Perdew, J. P.; Wang, Y. *Phys. Rev.* **1992**, *B45*, 13244) were employed with a DND basis and thermal (0.020 Ha) orbital occupation. The calculations were spin-unrestricted. DND is a double-numeric atomic basis with polarization functions for non-hydrogen atoms. Vibrational analysis confirmed that the reported structures were minima.

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