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Electron Transfer Competes with Proton Transfer in Gas-Phase Acid-Base Reactions

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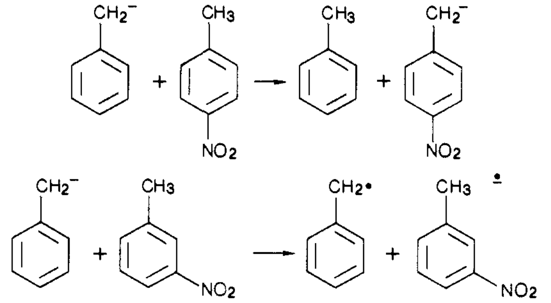
Single electron transfer (SET) processes have been implicated in a wide variety of reactions, especially those of carbanions.[1-4] The connection between SET and other reactions, particularly S_N2 and proton transfer, has long been noted and has recently been analyzed and reviewed comprehensively by Pross.[5,6] The mechanism of apparent proton transfer resulting from a combination of electron transfer followed by hydrogen atom transfer has been discussed previously,[7] and a combination of electron transfer and proton transfer has been suggested as the source of an unprecedented kinetic isotope effect in an apparent hydrogen atom transfer reaction.[8] One of the most striking aspects of the relationship between electron transfer and proton transfer appears in the work of Guthrie,[9] in which the competition between these pathways in carbanion chemistry is clearly displayed. In this communication we report a competition between electron transfer and proton transfer in a gas-phase ionic system where the channels must be very similar in energy. At least for some of the systems reported here, the proton-transfer reaction itself may be an example of electron transfer/hydrogen atom transfer (ET/HAT).

Reaction rates of substituted toluenes (perdeuterio, 3-trifluoromethyl, 3-cyano, 3,5-bis(trifluoromethyl), 4-cyano, 3-nitro, 4-nitro) with benzyl anion (generated from benzyltrimethylsilane plus fluoride ion) were measured with a pulsed ion cyclotron resonance (ICR) spectrometer.[10] The purpose of these experiments was to explore the validity of a Marcus theory analysis[11-13] of the effect of exothermicity on these proton-transfer reaction rate constants.[14] In general, we find the theory to be applicable; more exothermic proton transfers are faster. The efficiencies ($k_{\text{rxn}}/k_{\text{collision}}$) range from 0.004 for toluene-d_8 to 0.7 for 3,5-bis(trifluoromethyl)toluene. A roughly constant intrinsic activation energy,[15] $\Delta E_0^* = 7$ kcal/mol, accommodates the data. In studying the nitrotoluenes, however, we observed that while 4-nitrotoluene, whose reaction is 24.5 kcal/mol exothermic, reacts to give proton transfer at about the collision rate as expected for such an exothermic reaction,[16] 3-nitrotoluene, whose proton-transfer reaction is 13.5 kcal/mol exothermic and whose efficiency is predicted to be about 0.3, gives essentially only electron transfer, producing the radical anion, eq 1. Some 3-nitrobenzyl anion is produced in this reaction system; control experiments show that most of this product arises from deprotonation of 3-nitrotoluene by F^-.



(1)

The electron affinities[17,18] of all of the relevant neutral species are very close ($PhCH_2^\bullet$, 19.9 kcal/mol; 3-nitrotoluene, 21.4 kcal/mol; 4-nitrotoluene, 20.5 kcal/mol). Thus, when collision complexes are formed with some 10-20 kcal/mol excess energy, there is ample energy available for electron transfer to occur, at least transiently.

Details of the proton-transfer process for 4-nitrotoluene remain unclear, however. The Marcus theory correlation of proton-transfer rate constants versus exothermicity suggests that the overall reaction exothermicity is important in determining the reaction barrier height. The results for 4-nitrotoluene are thus consistent with either a one-step proton transfer or electron transfer[19] followed by hydrogen atom transfer, since the barrier would be lowered similarly for each of these exothermic processes.[20]

On the basis of the Marcus theory correlation, we predict that the overall proton-transfer channel for 3-nitrotoluene could be slow enough (efficiency = 0.3) that a competing reaction could be dominant. Indeed, the major process is electron transfer from benzyl anion to 3-nitrotoluene in the collision complex followed by dissociation of the complex to separated products. Thus, hydrogen atom transfer from the radical anion of 3-nitrotoluene to benzyl radical does not compete effectively with dissociation of the complex and must therefore have an appreciable barrier. With the more exothermic 4-nitrotoluene, if electron transfer/hydrogen atom transfer (ET/HAT) does occur, the hydrogen atom transfer is sufficiently fast owing to the exothermicity, that overall proton transfer is all that is observed. Alternatively, electron transfer may occur reversibly and merely be a side equilibrium which does not lead to products. For the other substituted toluenes, even if electron-transfer products were to occur transiently, formation of these separated electron-transfer products is endothermic and thus is not observed.

One can view the electron-transfer reactions as a consequence of the unusually high electron affinities of the nitrotoluenes and thus a unique channel which is only available in this case. In this picture, ET/HAT is not a general path but is seen only in special circumstances. For example, in the thermoneutral identity reaction of toluene with benzyl anion, the ET/HAT path is very unlikely;

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(1) The seminal work of Russell and co-workers is especially relevant: Russell, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* **1964**, *86*, 1807. Russell, G. A.; Janzen, E. G. *J. Am. Chem. Soc.* **1967**, *89*, 300. Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 5663; **1968**, *90*, 347.

(2) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734.

(3) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

(4) Review: Kochi, J. *Organometallic Mechanism and Catalysis*; Academic Press: New York, 1978.

(5) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212. This paper contains an excellent review of the field and an especially cogent description of some of the issues.

(6) See, also: Pross, A.: Shaik, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 187. Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363.

(7) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. Jordan, R. F.; Norton, J. R. In *Mechanistic Aspects of Inorganic Reactions*; Rorabacher, D. B., Endicott, J. F., Eds.; American Chemical Society: Washington, DC, 1982; ACS Symp. Ser. 198, p 403. Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945.

(8) Binstead, R. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 3287.

(9) Guthrie, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 6201. Guthrie, R. D.; Weisman, G. R.; Burdon, L. G. *J. Am. Chem. Soc.* **1974**, *96*, 6955. Guthrie, R. D.; Weisman, G. R. *J. Am. Chem. Soc.* **1974**, *96*, 6962. See, also: Guthrie, R. D.; Nutter, D. E. *J. Am. Chem. Soc.* **1982**, *104*, 7478.

(10) McIver, R. T., Jr. *Rev. Sci. Instrum.* **1978**, *49*, 111. McIver, R. T., Jr.; Hunter, R. L.; Ledford, E. B., Jr.; Locke, M. J.; Francl, T. J. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 65.

(11) Brauman, J. I.; Dodd, J. A.; Han, C.-C. In *Nucleophilicity*; Harris, J. M., McManus, S. P., Eds.; Advances in Chemistry 215; American Chemical Society: Washington, DC, 1987; p 22.

(12) Dodd, J. A.; Brauman, J. I. *J. Phys. Chem.* **1986**, *90*, 3559.

(13) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 2672.

(14) Dodd, J. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 5356.

(15) This is calculated on the basis of a constant well depth of 12 kcal/mol. For a discussion of the effects of well depths on these barrier estimations, see ref 12. An alternative Marcus description (ref 12) gives E°_{diff} (the intrinsic energy difference between the entrance channel and the reaction barrier) = 5 kcal/mol. The important factor is that of a constant intrinsic barrier, which seems to be true in this case.

(16) This reaction system proved somewhat difficult to study and frequently produced erratic results. The reaction, however, is unquestionably very fast.

(17) Drzaic, P. S.; Brauman, J. I. *J. Phys. Chem.* **1984**, *88*, 5285. Review: Wetzel, D. M.; Brauman, J. I. *Chem. Rev.* **1987**, *87*, 607.

(18) Grimsrud, E. F.; Caldwell, G.; Chowdhury, S.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 4627. Review: Kebarle, P.; Chowdhury, S. *Chem. Rev.* **1987**, *87*, 513.

(19) Guthrie, ref 9, has shown that electron transfer can be much faster than proton transfer, even for alcohols protonating carbanions.

(20) The one-step proton-transfer process may have a significant single electron transfer component, as discussed by Pross, ref 5.

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electron transfer is at least 20 kcal/mol endothermic, the toluene radical anion being unbound in the gas phase. For most of the benzylic systems we have examined, the ET step is endothermic, although the energy released in forming the collision complex may still allow it to occur. It is possible that the direct proton transfer and the ET/HAT paths would have different isotope effects,[21] but low-pressure gas-phase ion-molecule experiments have usually been unable to reveal such details because of the chemical activation aspects of the dynamics.[22]

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

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[21] Wellman, K. M., Victoriano, M. E.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 2242. Noest, A. J.; Nibbering, N. M. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *34*, 383. These authors have been able to measure small kinetic isotope effects for bimolecular reactions.

[22] Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 2906. This paper contains a discussion of some of the difficulties in interpreting kinetic isotope effects for these kinds of reactions.

Cyclodextrin Sandwiched Fe_4S_4 Cluster

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Since Holm and co-workers first reported the synthetic Fe_4S_4 type cluster mimicking the active site core of ferredoxin, the chemical and physical properties of these synthetic clusters have been extensively investigated.[1] These synthetic clusters, however, are usually unstable in an *aqueous* solution because of their facile hydrolytic degradations,[2] quite contrary to the natural ferredoxins.[3] Therefore, their redox reactivities in aqueous solution have been investigated only under the limited conditions where micelles,[4] bilayer membranes,[5] or high concentration of mercaptans[2,6] were used as the stabilizing cofactor. In the present paper, we wish to report the synthesis and redox reactivities of a new type of the synthetic clusters, **2** and **3**, which are stable in an aqueous solution without any additional stabilizing reagents and have the hydrophobic recognition site of cyclodextrin.[7]

6A,6D-Biphenyl-4,4′-disulfonyl-capped β-cyclodextrin was converted to the target cluster **2** via dimercaptan **1** by the ligand exchange reaction[8] under the conditions listed in Chart I.[9] The product (114 mg, 83% yield) was analyzed as a tetrahydrate.[10]

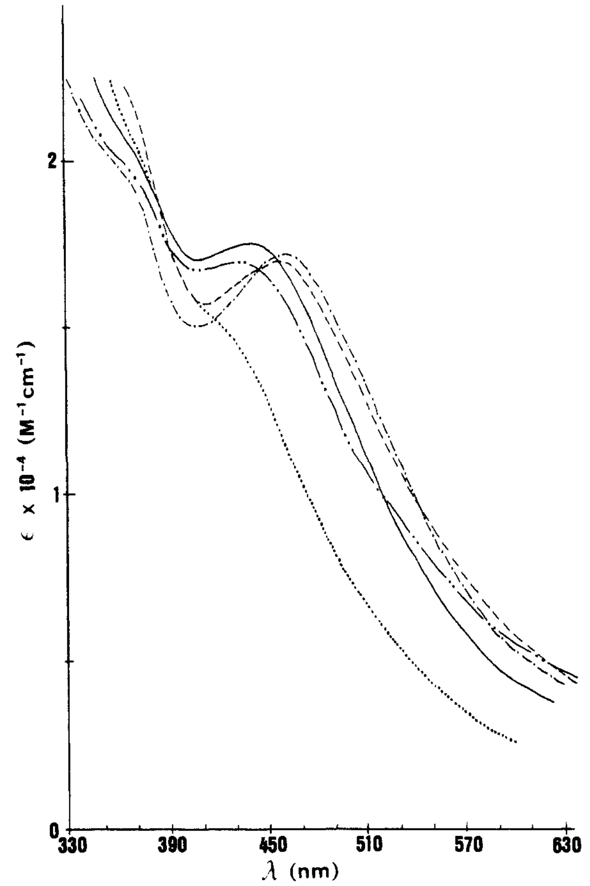
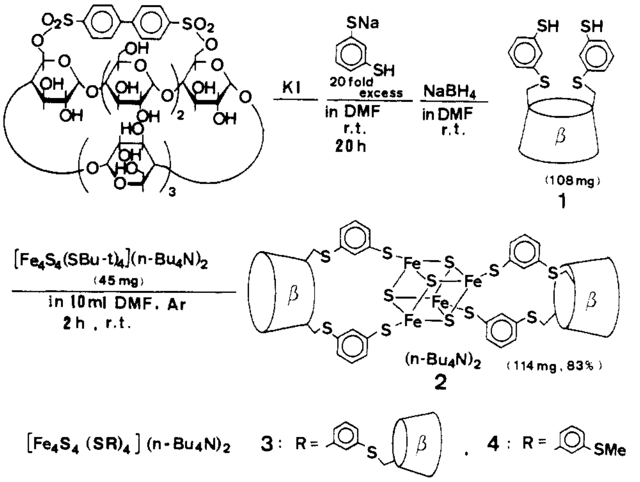


Figure 1. Electronic spectra of **2** (—), **3** (– – –), **4** (–··–) in DMF solution, **2** (—··—) in the 10 mM phosphate buffer (pH 7.0) (cell length = 1 cm), and **2** (···) electrolyzed at −1.15 V versus Ag/AgCl electrode in the DMF solution containing 0.1 M *n*-Bu_4NBr supporting electrolyte at 25 °C under Ar (cell length = 0.05 cm, see ref 11).

Chart I



The reference compounds **3** and **4** were also prepared by the similar ligand exchange reaction.

Physical properties of **2**, **3**, and **4** are summarized in Table I and Figure 1. As shown in Figure 1, the electronic spectra of **2**, **3**, and **4** exhibit the typical absorption bands of the Fe_4S_4 cluster (λ_{max} (nm) (ε) (DMF) **2**: 369 (sh, 20 700), 441 (17 500); **3**: 374 (sh, 20 300), 458 (17 000); **4**: 364 (sh, 19 600), 463 (17 300)). The reduction potentials of **2**, **3**, and **4** in DMF measured by a cyclic voltammetry were −0.94, −0.93, and −0.92 V versus Ag/AgCl at 25 °C, respectively. The reduced form of **2**, which was easily generated by using the thin-layer spectroelectrochemical cell reported by Saveant et al.,[11] reproduced the oxidized form

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† Deceased on March 22, 1987.

[1] Berg, J. M.; Holm, R. H. *Iron–Sulfur Proteins*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1983; Vol. IV, Chapter 1.

[2] (a) Bruice, T. C.; Moskiewicz, R.; Job, R. C. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 231. (b) Job, R. C.; Bruice, T. C. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2478.

[3] Lode, E. T.; Murray, C. L.; Rabinowitz, J. C. *J. Biol. Chem.* **1976**, *251*, 1675.

[4] (a) Tanaka, K.; Tanaka, T.; Kawafune, I. *Inorg. Chem.* **1984**, *23*, 516. (b) Tabushi, I.; Kuroda, Y.; Sasaki, Y. *Tetrahedron Lett.* **1986**, *27*, 1187.

[5] Tanaka, K.; Masanaga, M.; Tanaka, T. *J. Am. Chem. Soc.* **1986**, *108*, 5448.

[6] Hill, C. L.; Renaud, J.; Holm, R. H.; Mortenson, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 2549.

[7] The iron–sulfur cluster using 6-mercapto-6-deoxy-β-cyclodextrin was reported previously. The pure cluster, however, was not isolated, and the details are not known except the reduction potential of the mixture in DMF. See: Siegel, B. *J. Inorg. Nucl. Chem.* **1979**, *41*, 609.

[8] (a) Bobrik, M. A.; Que, L., Jr.; Holm, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 285. (b) Averill, B. A.; Herskovitz, T.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 3523.

[9] For the reactions of capped cyclodextrin derivatives, see: (a) Tabushi, I.; Yamamura, K.; Nabeshima, T. *J. Am. Chem. Soc.* **1984**, *106*, 5267. (b) Tabushi, I.; Kuroda, Y.; Mochizuki, A. *J. Am. Chem. Soc.* **1980**, *102*, 1152.

[10] Found (calcd for $C_{140}H_{224}N_2O_{66}S_{12}Fe_4 \cdot 4H_2O$) C: 45.63 (45.80), H: 6.56 (6.37), N: 0.72 (0.76), Fe: 5.8 (6.08). The molecular weight measured by the light scattering method is (3.7 ± 0.2) × 10^3 (calcd 3671.35). For the light scattering method, see: Huglin, M. B. *Light Scattering from Polymer Solutions*; Academic Press: New York, 1972.

0002-7863/88/1510-4049$01.50/0