iodeprotonation run was opened, and the contents (1.2 mL) were syringed into a flask containing ca. 10 g of polyphosphoric acid (PPA). The reaction of PPA with CHA proceeded slowly, and the flask was heated gently for 1 h. The hydrocarbons were then vacuum transferred from the flask into an NMR tube containing CsCHA and [¹H]CHA, and the detritiation reaction was monitored at 297 K. The measured rate constants are tabulated in Table I. All of the rate constants refer to rates/hydrogen.

It can be shown that our tritiodeprotonation and protiodetritiation rates are directly comparable, because they result from tracer experiments. The average rate of exchange of cubane is then 0.0060 times that of the ring position in *p*-xylene. Since this position exchanges 0.11 times as fast as benzene,[1] the kinetic acidity of cubane is 6.6×10^{-4} that of benzene. Figure 1 shows that its acidity (6.3×10^4 times that of cyclohexane) is still, however, almost 5 times that predicted from $^1J_{CH}$ values (1.3×10^4 times that of cyclohexane), indicating that there is indeed an enhanced acidity for cubane, but it is much smaller than previously reported. Our result thus supports the enhanced rehybridization effect shown by the calculations. Cubane is also kinetically less acidic than cyclopropane (7.1×10^4 times the kinetic acidity of cyclohexane),[5] which is qualitatively correct on the basis of s character (31% for cubane vs 32% for cyclopropane). Additional experiments and calculations are in progress to further define the relationships between thermodynamic and kinetic acidities on related systems.

Surprising Differences in the Reactivity of Cyanoaromatic Radical Anions Generated by Photoinduced Electron Transfer

Matthew A. Kellett and David G. Whitten*

*Department of Chemistry, University of Rochester
Rochester, New York 14627*

Ian R. Gould

*Corporate Research Laboratories
Eastman Kodak Company, Rochester, New York 14650*

William R. Bergmark

*Department of Chemistry, Ithaca College
Ithaca, New York 14850*

Cyanoaromatics such as 9,10-dicyanoanthracene (DCA) are widely used as "sensitizers" in photochemical electron transfer reactions.[1-17] Although it is generally accepted that the excited

cyanoaromatics undergo single electron transfer (SET) reduction to generate the corresponding anion radicals (and these anion radicals are frequently observed, as intermediates, via laser flash photolysis techniques),[8,9] the reported fate of the cyanoaromatic can be quite varied, depending upon the other reagents present. Thus in some cases, they may function as true sensitizers with no net consumption,[2] such as in a number of cases where strained hydrocarbons are induced to rearrange via photochemical SET.[3] In other instances, the cyanoaromatics undergo net reactions as diverse as substitution,[1] addition, or net two-electron reduction to the corresponding dihydro compounds.[18] In several cases it is clear that the cyanoaromatic anion radical, or some species derived from it, must be undergoing reaction with reagents that are normally regarded as relatively unreactive. In this paper, we report some studies that indicate that the reactivity of photogenerated cyanoaromatic anion radicals is strongly affected by the medium in which they are generated; interestingly we report conditions under which potentially reactive anion radicals of DCA and 2,6,9,10-tetracyanoanthracene (TCA) can be the stable "end products" of photoinduced redox reactions.

In 1979 Ohashi et al.[19] described a remarkable reaction in which DCA was converted into 9-amino-10-cyanoanthracene and acetaldehyde when irradiated in the presence of amines and water in acetonitrile solvent. Related chemistry was subsequently explored by Mariano et al.[20] Although a precise mechanism has not been established, it was determined that the amino nitrogen came from acetonitrile and, given the low reactivity of acetonitrile toward nucleophiles, that a highly reactive intermediate had to be involved. We have found that the simple addition of an inert salt suppresses this reaction and 9,10-dicyanoanthracene radical anion (DCA⁺⁻) is produced as a stable final product. A number of reports[21-23] indicate that added salts dramatically enhance the lifetime (and reduce the reactivity) of radical ions. This may be in part a medium effect, but the major effect is the stabilization of the radical ion by the presence of a stable, unreactive counterion. When a vacuum-degassed solution of DCA (1.22×10^{-4} M), triethylamine (0.22 M), and tetra-*n*-butylammonium dihydrogen phosphate (5.4×10^{-3} M) is irradiated with a 450-W medium-pressure mercury lamp filtered to pass light from 370 to 440 nm, the characteristic absorption spectrum[24] of DCA radical anion appears and is stable for weeks at a time. The fate of triethylamine is not clear except for NMR evidence that can be assigned to diethylamine.[25] When oxygen is admitted, the radical anion is quickly converted back to DCA. The conversion of DCA to stable DCA radical anion is not complete and of low quantum yield, however, and depends on a number of experimental variables. For example, both the quantum and chemical efficiency of radical ion

(1) Arnold, D. R.; Du, X. *J. Am. Chem. Soc.* **1989**, *111*, 7666.
(2) Popielarz, R.; Arnold, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 3068.
(3) Gassman, P. G. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C, p 70.
(4) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80.
(5) Arnold, D. R.; Wong, P. C.; Maroulis, A. J.; Cameron, T. S. *Pure Appl. Chem.* **1980**, *52*, 2609.
(6) Lewis, F. D.; Petisce, J. R. *Tetrahedron* **1986**, *42*, 6207.
(7) Albini, A.; Spreti, S. *Tetrahedron* **1984**, *40*, 2975.
(8) Reichel, L. W.; Griffin, G. W.; Muller, A. J.; Das, P. K.; Ege, S. *Can. J. Chem.* **1984**, *62*, 424.
(9) Davis, H. F.; Das, P. K.; Reichel, L. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 6968.
(10) Eaton, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 3278.
(11) Lan, J. Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 6710.
(12) Mizuno, K.; Terasaka, K.; Yasueda, M.; Otsuji, Y. *Chem. Lett.* **1988**, 145.
(13) Mizuno, K.; Tamai, T.; Nakanishi, I. *Chem. Lett.* **1988**, 2065.
(14) Lopez, L.; Troisi, L.; Rashid, S. M. K.; Schaap, A. P. *Tetrahedron Lett.* **1989**, *30*, 485.

(15) Ohashi, M.; Miyaki, K.; Tsujimoto, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1683.
(16) Sulpizio, A.; Albini, A.; d'Alessandro, N.; Fasani, E.; Pietra, S. *J. Am. Chem. Soc.* **1980**, *111*, 5773.
(17) Lewis, F. D.; Zebrowski, B. E.; Correa, P. E. *J. Am. Chem. Soc.* **1984**, *106*, 187.
(18) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1986**, *108*, 7356.
(19) Ohashi, M.; Kudo, H.; Yamada, S. *J. Am. Chem. Soc.* **1979**, *101*, 2201.
(20) Hasegawa, E.; Brumfield, M. A.; Mariano, P. S. *J. Org. Chem.* **1988**, *53*, 5435.
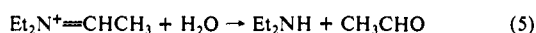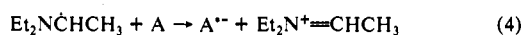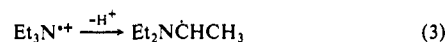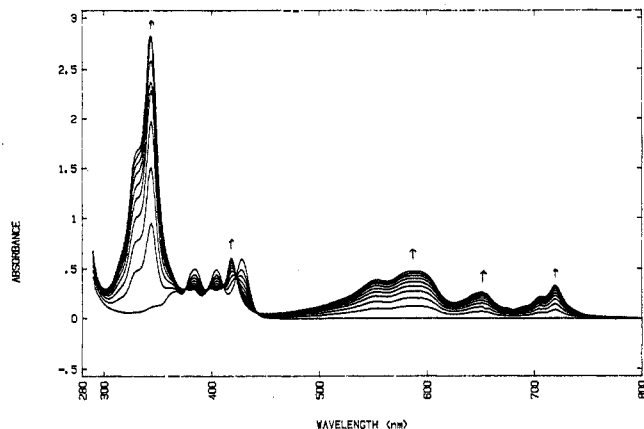(21) Arnold, D. R.; Snow, M. S. *Can. J. Chem.* **1988**, *66*, 3012.
(22) Goodson, B.; Schuster, G. B. *Tetrahedron Lett.* **1986**, *27*, 3123.
(23) Mizuno, K.; Ichinose, N.; Tamai, T.; Otsuji, Y. *Tetrahedron Lett.* **1985**, *26*, 5823.
(24) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.
(25) The overall chemistry with triethylamine is summarized in eqs 1–5 (A = DCA, TCA):

$$A \xrightarrow{h\nu} A^{1*} \qquad (1)$$

$$A^{1*} + Et_3N \rightarrow A^{\cdot-} + Et_3N^{\cdot+} \qquad (2)$$

$$Et_3N^{\cdot+} \xrightarrow{-H^+} Et_2N\dot{C}HCH_3 \qquad (3)$$

$$Et_2N\dot{C}HCH_3 + A \rightarrow A^{\cdot-} + Et_2N^+{=}CHCH_3 \qquad (4)$$

$$Et_2N^+{=}CHCH_3 + H_2O \rightarrow Et_2NH + CH_3CHO \qquad (5)$$

Figure 1. Absorbance spectra observed upon photolysis of tetracyano-anthracene (TCA) in acetonitrile in the presence of *meso*-1,2-diphenyl-1,2-diaminoethane showing the formation of TCA$^{\cdot-}$ and the disappearance of TCA.

formation is greatly enhanced by the addition of water (10% by volume). The maximum yield noted was 91%. These results indicate that with additional stabilization of the radical anion the Ohashi reaction no longer takes place.

A similar result was obtained for TCA with triethylamine but without added salt. Thus irradiation of an acetonitrile solution of TCA (5×10^{-5} M) and triethylamine (1×10^{-3} M) leads to the disappearance of TCA with the concurrent appearance of an intense blue color and complex absorption spectrum with a clean isosbestic point. Although the quantum efficiency is low, irradiation can be continued until all the TCA has been converted. Admitting oxygen regenerates the TCA without detectable loss.[26] The radical anion was identified by its ESR spectrum. It can also be prepared electrochemically with the same characteristic absorption spectrum. The TCA radical anion is completely stable under these conditions for weeks. It is also stable under conditions of added water (up to 50% v/v) and in the presence of acetic anhydride. In the case with acetic anhydride, diethylacetamide is identified through GC–MS, which again suggests that the triethylamine is converted to diethylamine, which is then trapped by the anhydride. TCA$^{\cdot-}$ is apparently not a strong base nor a good nucleophile under these circumstances. The reaction appears to be quite general for amines.[25] When *meso*-1,2-diphenyl-1,2-diaminoethane (*meso*-DPED) is irradiated with TCA under similar conditions, TCA$^{\cdot-}$ is formed (Figure 1), along with benzaldehyde, a product of a fragmentation reaction characteristic of 1,2-diamines.[27] If the reaction is carried out in the presence of oxygen, the TCA is not consumed and acts as a true "sensitizer" for the oxidative fragmentation reaction.

Additional information can be obtained from transient absorption spectroscopy. Pulsed laser excitation of acetonitrile solutions of DCA or TCA in the presence of 0.05 M triethylamine, with 0.15 M biphenyl as a cosensitizer,[24] results in rapid (<20 ns) production of DCA$^{\cdot-}$ or TCA$^{\cdot-}$ absorbance, followed by a slower growth of an absorbance that is equal to that formed rapidly, on a microsecond time scale. The rapid formation is evidently the result of the initial electron transfer between biphenyl and cyanoaromatic. The slower formation is attributed to reduction of a second ground-state cyanoaromatic by the iminium radical formed by oxidation of TEA (TEA + Bp$^+$ → TEA$^{\cdot+}$ + Bp) and deprotonation of the so-formed TEA$^{\cdot+}$.[28] Similar two-stage redox reactions have been noted in other systems.[29] The

cyanoanthracene radical anions are not observed to undergo any decay even on a time scale of milliseconds.

One of the most important of the many factors that control the reactivity of photochemical SET generated ion radicals is solvent polarity. A closely coupled question is whether the primary intermediate is a solvent-separated radical ion pair (SSRIP) or a contact radical ion (CRIP). The SSRIP are more stable than CRIP in polar solvents ($\epsilon > 7$),[30] and in these solvents the highly solvated ion radicals can separate to form free radical ions. Thus under these conditions the anion radicals are potentially less reactive with the radical cations (as bases and nucleophiles) than in nonpolar solvents, in which the CRIP are more important. For the CRIP the lower solvation and close proximity of the ion radicals can result in higher reactivity, especially toward each other. Thus we find that irradiation of DCA (1×10^{-4} M) in acetonitrile with the amino ketone 3-methyl-3-(4-morpholinyl)-2-butanone (0.025 M) and tetra-*n*-butylammonium phosphate (7×10^{-3} M) yields DCA$^{\cdot-}$ as a stable (in the absence of O$_2$) product (80% yield) and very little 4-acetylmorpholine, the major product from radical cation–radical anion reaction. In contrast, irradiation in benzene, where 4-acetylmorpholine is produced in >80% yield, leads to no detectable stable anion radical, even on prolonged photolysis.[31] Similarly, irradiation of TCA in benzene with various diamines leads only to fragmentation and disappearance of TCA (presumably to TCAH$_2$) but not to stable TCA$^{\cdot-}$, in contrast to the results described above for acetonitrile. These results reinforce that the reactivity of ion radicals generated by photoinduced electron transfer can be strongly altered by the choice of solvent and/or added solutes; while the present results focus on attenuation of anion radical reactivity, it seems clear that similar modification of cation radical reactivity can be readily obtained for other donor–acceptor combinations.

(30) Weller, A. *Z. Phys. Chem.* (*Munich*) **1982**, *133*, 93.

(31) No salt was present in the product studies. Addition of salt to benzene solutions does not lead to detection of TCA$^{\cdot-}$.

Stereochemical Studies on the Atomic Inversion of Divalent Oxygen: The Use of Dinaphtho[a,j]anthracenes To Restrict Rotational Motion[1]

Ram B. Gupta[2] and Moses K. Kaloustian*

Department of Chemistry, Fordham University
Bronx, New York 10458

Richard W. Franck*

Department of Chemistry, Hunter College
City University of New York, New York, New York 10021

John F. Blount

Chemical Research Department, Hoffman LaRoche Inc.
Nutley, New Jersey 07110

Received September 10, 1990

The barrier to atomic inversion ("linearity barrier") at ether oxygen[3] is not known; the rotational barrier about the C–O bond, in contrast, is well documented.[4] According to the calculations

(26) The regeneration reaction is presumably electron transfer from TCA$^{\cdot-}$ to oxygen to form O$_2$$^{\cdot-}$. This process is endothermic by ca. 0.4 eV but may occur on a time scale of seconds.

(27) Kellett, M. A.; Whitten, D. G. *J. Am. Chem. Soc.* **1989**, *111*, 2314.

(28) The second stage of the redox reaction (eq 4) is favorable by ca. 0.7 eV. The iminium radical oxidation potential is −1.12 V while the reduction potential of the ground-state TCA is −0.45 V. Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

(29) Monserrat, K.; Foreman, T. K.; Grätzel, M.; Whitten, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 6667.

(1) Presented at the 197th National Meeting of the American Chemical Society, Dallas, TX, April 1989; ORGN 255.

(2) Current address: Research Laboratories, American Cyanamid Co., 1937 West Main St., Stamford, CT, 06904.

(3) One may distinguish between the following types of ether oxygen: C_{sp3}–O–C_{sp3}, C_{sp3}–O–C_{sp2}, and C_{sp2}–O–C_{sp2}.