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Generation of Tris(dialkylamino)cyclopropenyl Radical Dications by Pulse Radiolysis and Redox Potential Determination for the $C_3(NEt_2)_3^{•2+}/C_3(NEt_2)_3^+$ and $C_3(NC_5H_{10})_3^{•2+}/C_3(NC_5H_{10})_3^+$ Couples

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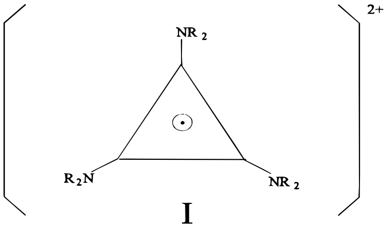
Pulse radiolysis experiments were carried out with neutral aqueous solutions of cyclopropenyl cations $C_3(NR_2)_3^+$, ($R_2 = Et_2$, C_5H_{10}) also containing bromide, iodide, or azide, to study possible one-electron transfer rates and equilibria involving $C_3(NR_2)_3^{•2+}/C_3(NR_2)_3^+$ couples. $Br_2^{•-}$ oxidized $C_3(NR_2)_3^+$ completely to the corresponding radical dication with rate constants of 2.1×10^8 ($R_2 = Et_2$) and 7.4×10^8 L mol^{-1} s^{-1} ($R_2 = C_5H_{10}$), whereas no reaction was detected between Br^- and $C_3(NR_2)_3^{•2+}$. In contrast, the $C_3(NR_2)_3^{•2+}$ radical was found to oxidize I^-, although no reaction was observed between $I_2^{•-}$ and $C_3(NR_2)_3^+$. With azide, however, the system reached equilibrium, $N_3^• + C_3(NR_2)_3^+ \rightleftarrows N_3^- + C_3(NR_2)_3^{•2+}$. From the equilibrium constants $K = 90$ ($R_2 = Et_2$) and $K = 280$ ($R_2 = C_5H_{10}$) and the known redox potential $E(N_3^•/N_3^-) = 1.35$ V, we calculate $E(C_3(NR_2)_3^{•2+}/C_3(NR_2)_3^+) = 1.23 \pm 0.04$ ($R_2 = Et_2$) and 1.20 ± 0.03 V ($R_2 = C_5H_{10}$) versus NHE.

Introduction

The chemistry of the cyclopropenyl group has received considerable attention. The structure and reactivity of this highly strained ring system are suited to theoretical as well as experimental investigation.[1−5] In addition to their fundamental appeal, the unusual vibronic properties predicted for cyclopropenyl radicals have stimulated interest in their potential for use as molecular electronic devices.[6] Cyclopropenyl species are normally isolated as monocations in which the parent cation $[C_3H_3]^+$ is the first member ($n = 0$) of the Huckel $(2 + 4n)\pi$ aromatic series. Studies of the synthesis and reactivity of cyclopropenyl radicals by reduction of their cationic counterparts illustrate the inherent difficulty associated with adding an electron to a closed-shell aromatic system.[2] Similarly, oxidation of a cyclopropenyl cation is expected to be energetically disfavored. Tris(dialkylamino)cyclopropenylium ions are remarkable exceptions to this rule. These electron-rich, readily oxidizable species give monoradical dications (**I**) of unusually high stability.[7] Charge delocalization involving the heteroatoms no doubt contributes to their stabilization. Tris(dialkylamino)cyclopropenyl radical dications have been prepared by chemical and electrochemical means and characterized in some detail.[7−9] Salts of these deep-red cations are easily handled and display interesting properties.[1,10] We now report the generation of tris(dialkylamino)-substituted cyclopropenyl radical dications by pulse radiolysis and describe how this technique was used to determine the redox potentials of $C_3(NR_2)_3^{•2+}/C_3(NR_2)_3^+$ couples for the first time.



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Experimental Section

All the materials were analytical grade reagents of the highest purity commercially available. Chloride salts of the tris(dialkylamino)cyclopropenylium cations were prepared by an established method.[5] Pulse radiolysis experiments were carried out with 0.2 μs pulses of 4 MeV electrons from a linear accelerator that delivers doses of 3−4 Gy/pulse. Water was purified by a Millipore Milli-Q system. Solutions were prepared just before each experiment and were deoxygenated by bubbling with nitrous oxide, which also reacts with the hydrated electron to increase the yield of $OH^•$ radicals. The oxidizing inorganic radicals were produced by rapid scavenging of the $OH^•$ radicals and used to oxidize the substrate molecules (S) to their radical cations ($S^{•+}$):

$$H_2O \rightsquigarrow e^-_{aq}, H^•, OH^•, H_2O_2, H_2, H_3O^+$$

$$e^-_{aq} + N_2O + H_2O \rightarrow OH^• + OH^- + N_2 \quad (1)$$

$$OH^• + X^-(N_3^-) \rightarrow OH^- + X^•(N_3^•) \quad (2)$$

$$X^• + X^- \rightleftharpoons X_2^{•-} \quad (3)$$

$$X_2^{•-}(N_3^•) + S \rightarrow S^{•+} + 2X^-(N_3^-) \quad (4)$$

The formation and reaction kinetics of the radicals were monitored at their absorption maxima: $Br_2^{•-}$, 360 nm; $I_2^{•-}$, 380 nm; $N_3^•$, 275 nm; $C_3(NEt_2)_3^{•2+}$, 480 nm; $C_3(NC_5H_{10})_3^{•2+}$, 529 nm. Kinetic parameters were obtained by curve fitting using the Marquardt alogirithm for nonlinear least squares. Time-resolved spectra of the radical species are presented as the product of the radiation chemical yield (G, μmol J^{-1}) and change in extinction coefficient relative to the absorbance of the nonoxidized parent compound ($\Delta\epsilon$, L mol^{-1} cm^{-1}).

Results and Discussion

The spectra and λ_{max} values for the cyclopropenyl radical dications produced by oxidation with $Br_2^{•-}$ and $N_3^•$ are shown in Figure 1 and are consistent with those presented before in less detail.[8]

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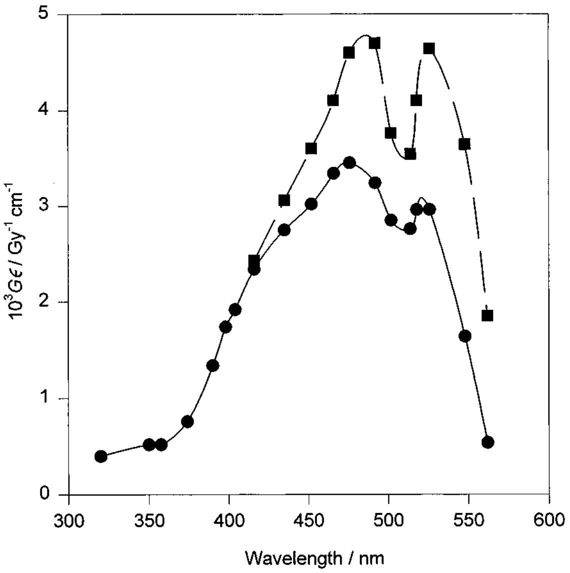

Figure 1. UV spectra of $C_3(NC_5H_{10})_3^{\bullet 2+}$ (■) and $C_3(NEt_2)_3^{\bullet 2+}$ (●) produced by pulse radiolysis of N_2O-saturated solutions of the cyclopropenyl chlorides (0.001 mol L^{-1}) and potassium bromide (0.1 mol L^{-1}).

The redox potentials of the pairs $X_2^{\bullet -}/2X^-$ (X = Br or I) and $N_3^\bullet/N_3^-$ have been estimated or determined by a number of groups using several different methods and collated into a fairly consistent set of values by Wardman:[11] $E(I_2^{\bullet -}/2I^-) = 1.03$ V, $E(Br_2^{\bullet -}/2Br^-) = 1.63$ V, and $E(N_3^\bullet/N_3^-) = 1.35$ V. Preliminary investigations suggested that $E([C_3(NR_2)_3]^{\bullet 2+}/[C_3(NR_2)_3]^+)$ might fall within this range of redox potentials, and therefore, we examined the possible reactions of $C_3(NR_2)_3^{\bullet 2+}$ or $C_3(NR_2)_3^+$ with these anions and radicals.

I^- + $C_3(NR_2)_3^+$ System. Addition of increasing concentrations of $C_3(NR_2)_3^+$ to solutions containing potassium iodide (0.1 mol L^{-1}) caused competition for the $OH^\bullet$ radicals but had no effect on the rate of decay of the $I_2^{\bullet -}$ absorption at 380 nm, showing that there is no reaction between $I_2^{\bullet -}$ and $C_3(NR_2)_3^+$. Conversely, the characteristic absorption of $I_2^{\bullet -}$ was also observed when I^- was added to a solution containing excess $C_3(NR_2)_3^+$, the rate of formation of $I_2^{\bullet -}$ in this case being exponential and proportional to I^- concentration. This is consistent with the reaction 5 followed by reaction 6, which is known to be much faster[15] (ca. 10^{10} M^{-1} s^{-1}), so that the overall reaction is reaction 7:

$$C_3(NR_2)_3^{\bullet 2+} + I^- \rightarrow C_3(NR_2)_3^+ + I^\bullet \quad (5)$$

$$I^- + I^\bullet \rightleftharpoons I_2^{\bullet -} \quad (6)$$

$$C_3(NR_2)_3^{\bullet 2+} + 2I^- \rightarrow C_3(NR_2)_3^+ + I_2^{\bullet -} \quad (7)$$

Br^- + $C_3(NR_2)_3^+$ System. In contrast to the iodide system, $Br_2^{\bullet -}$ reacted completely with $C_3(NR_2)_3^+$ to give the radical dication whose rate of formation was exponential and first-order in $C_3(NR_2)_3^+$. Second-order rate constants of $k = (2.1 \pm 0.2) \times 10^8$ L mol^{-1} s^{-1} ($R_2 = Et_2$) and $k = (7.4 \pm 0.7) \times 10^8$ L mol^{-1} s^{-1} ($R_2 = C_5H_{10}$) are consistent with the reaction 8:

$$Br_2^{\bullet -} + C_3(NR_2)_3^+ \rightarrow 2Br^- + C_3(NR_2)_3^{\bullet 2+} \quad (8)$$

There was no evidence for $C_3(NR_2)_3^{\bullet 2+}$ oxidizing Br^-, i.e., no evidence for a redox equilibrium.

N_3^- + $C_3(NR_2)_3^+$ System. Addition of $C_3(NR_2)_3^+$ to solutions containing sodium azide was accompanied by two effects. Competition for the $OH^\bullet$ radicals caused a decrease in the initial $N_3^\bullet$ radical concentration produced by the pulse, and additionally, the decay of $N_3^\bullet$ radicals became much faster in the presence of $C_3(NR_2)_3^+$ but still followed pseudo-first-order kinetics. The first experiment indicated that $N_3^\bullet$ oxidizes $C_3(NR_2)_3^+$ with a rate constant on the order of 10^8 L mol^{-1} s^{-1}. When the concentration of N_3^- was adjusted to 0.2 mol L^{-1} and that of $C_3(NR_2)_3^+$ to 1 mmol L^{-1}, it became apparent that $N_3^\bullet$ does not decrease to zero in the initial first-order process. Instead, a plateau value remains that then decays much more slowly, probably by a second-order process. A similar plateau value, less than the initial absorption maximum, is seen when monitoring the formation and decay of $C_3(NR_2)_3^{\bullet 2+}$. These plateau levels and the kinetics leading to them depend on the concentrations of both N_3^- and $C_3(NR_2)_3^+$ as expected for the equilibrium reaction 9

$$N_3^\bullet + C_3(NR_2)_3^+ \rightleftharpoons N_3^- + C_3(NR_2)_3^{\bullet 2+} \quad (9)$$

The value of K_9 for this reaction was found by establishing the concentrations of all species involved in the equilibrium relative to the absorption characteristic of each species on its own. Data were collected at either 480 nm ($R_2 = Et_2$) or 529 nm ($R_2 = C_5H_{10}$) for a range of $C_3(NR_2)_3^+$ and N_3^- concentrations. $N_3^\bullet$ does not absorb light at these wavelengths, and therefore, its contribution to the absorption was always equal to zero. Averages of a series of experiments yielded $K_9 = 90 \pm 50$ ($R_2 = Et_2$) and 280 ± 10 ($R_2 = C_5H_{10}$). These values give $\Delta E = -(RT/F)\ln K = 0.12 \pm 0.02$ and 0.146 ± 0.001 V for differences in redox potentials between the azide and cyclopropenyl systems. From $E(N_3^\bullet/N_3^-) = 1.35$ V[12] we calculate $E(C_3(NEt_2)_3^{\bullet 2+}/C_3(NEt_2)_3^+) = 1.23 \pm 0.04$ V and $E(C_3(NC_5H_{10})_3^{\bullet 2+}/C_3(NC_5H_{10})^+) = 1.20 \pm 0.03$ V vs NHE.

1,3,5-Tris(dialkylamino)benzene is a species akin to the tris(dialkylamino)-substituted cyclopropenylium ion. Each is comprised of an aromatic carbocycle symmetrically substituted by excellent π electron donors. Furthermore, the nitrogens of both systems are fully alkylated, which precludes the possibility of their existing in nonbenzenenoid tautomeric forms. Huckel molecular orbital calculations predict that the HOMO of the tris(dialkylamino)cyclopropenylium cation should fall in the same energy range as the degenerate HOMOs of neutral 1,3,5-tris(dialkylamino)benzenes,[8] which notoriously behave as electron-rich and readily oxidizable compounds.[13] On this basis, it might be expected that the values of the one-electron oxidation potential would be similar for the two systems. Oxidation half-wave potentials of several tris(dialkylamino)-substituted benzenes have been measured using the polarographic method.[13] The values were determined in acetonitrile against a silver—silver ion (10^{-2} mol L^{-1}) reference electrode, which is 0.51 V [14] relative to the NHE. Referenced against the NHE, half-wave one-electron oxidation potential values of 1,3,5-tris(dialkylamino)benzenes range from 0.52 to 0.86 V, somewhat less than for the kindred cyclopropenylium ions. 1,3,5-Tripiperidino-substituted benzene is a close analogue of the tris(piperidino)cyclopropenylium ion, and the difference of these couples is about 0.5 V (1.20−0.69 = 0.51 V). Even when allowance is made for the fact that the two couples were determined in different solvents, this difference remains significant.

Intuitively, a larger one-electron oxidation potential for the cyclopropenylium system might be expected because an electron is being removed from an already positively charged parent. Our results confirm this and imply factors other than the energy level of the HOMO from which the electron is lost are important, particularly in an aqueous environment.

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References and Notes

(1) Weiss, R.; Grimmeis, A. M. H. *Z. Naturforsch.* **1991**, *46b*, 104.

(2) Deycard, S.; Hughes, L.; Lusztyk, J.; Ingold K. U. *J. Am. Chem. Soc.* **1987**, *109*, 4954.

(3) Chipman, D. M.; Miller, K. E. *J. Am. Chem. Soc.* **1984**, *106*, 6236.

(4) Byun, Y.-G.; Saebo, S.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1991,** *113*, 3689.

(5) Clark, G. R.; Surman, P. W. J.; Taylor, M. J. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1523.

(6) Tachibana, A.; Asai, Y.; Ikeuchi, S.; Ishikawa, S.; Yamabe, T. *Theor. Chim. Acta* **1990**, *78*, 1.

(7) Gerson, F.; Plattner, G.; Yoshida, Z. *Mol. Phys.* **1971**, *21*, 1027.

(8) Weiss, R.; Shloter, K. *Tetrahedron Lett.* **1975**, *40*, 3491.

(9) Taylor, M. J.; Clark, G. R.; Surman, P. W. J. *J. Chem. Soc., Chem. Commun.* **1994**, 2517.

(10) Weiss, R.; Grimmeiss, A. M. H. *Z. Naturforsch.* **1989**, *44b*, 1447.

(11) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1711.

(12) Alfassi, Z. B.; Harriman, A.; Huie, R. E.; Mosseri, S.; Neta, P. *J. Phys. Chem.* **1987**, *91*, 2120.

(13) Effenberger, F. *Acc. Chem. Res.* **1989**, *22*, 27.

(14) Larson, R. C.; Iwamoto, R. T.; Adams, R. N. *Anal. Chim. Acta* **1961**, *25*, 371.

(15) Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; J. Wiley and Sons, Inc.: New York, 1961; Chapter 7.