remains below free spin, being ca. 1.98 in Ag_3^{2+} and ca. 1.97 in Ag_4^{3+}. These facts enable us to discard distorted Ag_4^+ and Ag_4^{3+} from the list of possibilities.

We turn to the pentanuclear clusters Ag_5^{2+} and Ag_5^{4+}. Our calculations predict for Ag_5^{2+} very similar behavior to that for Ag_4^+: the unpaired spin resides predominantly on the apical nuclei. This conclusion confirms that of Ozin, Mattar, and McIntosh,[14] who predicted for Ag_5^{2+} apical ^{109}Ag hyperfine interactions of ca. 600 MHz. Clearly, hyperfine interactions of this magnitude are inconsistent with the observed spectrum, and we can discard the possibility that our spectrum is due to Ag_5^{2+}.

We are left with Ag_5^{4+}. Our calculations predict, for an equilateral triangular biprism, 2.85 Å on a side, spin populations in Ag 5s atomic orbitals of 0.204 for the three equatorial atoms, but only 0.086 for the two apical atoms. Silver atoms (^{109}Ag, $5^2S_{1/2}$) in the gas-phase have a hyperfine interaction of 1977 MHz,[15] so that the above spin populations correspond to ca. 400 MHz for the three equatorial nuclei and ca. 170 MHz for the two apical nuclei.

These calculations on Ag_5^{4+} are similar in some respects to the predictions of Ozin, Mattar, and McIntosh,[14] who obtained (for ^{109}Ag) isotropic hyperfine interactions of 350 and 200 MHz respectively for the equatorial and apical nuclei. They also predicted with remarkable accuracy the g factors of Ag_5^{4+}: $g_\parallel = 2.015$, $g_\perp = 2.047$. Thus, we see that an assignment of the observed spectrum to Ag_5^{4+} cannot be lightly dismissed: both the predicted **g** tensor and the hyperfine interactions of the equatorial silvers agree quite well with the measurements. There is, however, a considerable overestimate of the participation of apical Ag 5s atomic orbitals in the SOMO. We estimate that the apical ^{109}Ag hyperfine interactions are close to 30 MHz rather than 200 MHz. Spectral simulations suggest $g = (2.0384, 2.0384, 2.02)$, $a_{109}(3) = (317, 305, 305\ \text{MHz})$, $a_{109}(2) \simeq (30, 30, 30\ \text{MHz})$, where tensor components are in the order x, y, z with z the direction of the threefold axis. There is, of course, considerable uncertainty in the hyperfine anisotropy extracted from an almost solution-like spectrum (Figure 2). Even slight anisotropy in silver hyperfine interactions translates[15] into considerable spin density in atomic 4d or 5p orbitals, however. This must account for the appreciable (50%) deficit in unpaired spin density indicated by the isotropic ^{109}Ag hyperfine interactions. Since the displacements of the **g** tensor components from the free-spin value are positive, one may conclude that Ag 4d make more important contributions than Ag 5p to the SOMO.

In contrast to the reaction with ammonia, which yielded a hexanuclear adduct, the reaction of the $Ag_6^+ \cdot 8Ag^+$ cluster with ethylene appears to result in the formation of a "naked" silver cluster. This conclusion was confirmed by the recent observations of Michalik and Kevan,[16] who obtained the same spectrum directly by H_2 reduction or γ-irradiation of AgNa-A sieves. Their suggestion that the carrier of the spectrum is Ag_3 appears to be untenable however, as we have seen.

A comparison of our conclusions with those of Seff and his co-workers indicates that much remains to be understood in the area of silver-zeolite chemistry. Seff's single-crystal X-ray data show conclusively that reaction of the $Ag_6 \cdot 8Ag^+$ cluster with ammonia results in the destruction of the cluster and the formation of N_3H_3 and N_3H_5. Our results perhaps indicate that the initial step in this process is ammonia attack on the Ag ions in the cube surrounding the Ag_6 cluster.

With ethylene, on the other hand, our results suggest the formation of a new cluster, probably Ag_5^{4+}. Seff's data indicate that the Ag_6 cluster is intact but that two Ag^+ ions have been lost from the surrounding cube of Ag^+ ions.

Registry No. $Ag_6^+ \cdot 8Ag^+$, 106928-96-5; Ag_5^{4+}, 106905-98-0; ammonia, 7664-41-7; ethylene, 74-85-1.

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The Redox Potential of the Azide/Azidyl Couple

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Pulse radiolysis experiments were carried out with neutral aqueous solutions containing azide with iodide, bromide, or thiocyanate to examine possible one-electron transfer rates and equilibria involving the $N_3^\bullet/N_3^-$ couple. The N_3 radical was found to oxidize I^- with a rate constant of $4.5 \times 10^8\ M^{-1}\ s^{-1}$. No reaction was observed between $I_2^{\bullet-}$ and N_3^-. With Br^-, however, the system reached equilibrium, $Br_2^{\bullet-} + N_3^- \rightleftharpoons 2Br^- + N_3^\bullet$, with $k_f = 4.0 \times 10^8\ M^{-1}\ s^{-1}$ and $k_r = 7.3 \times 10^3\ M^{-2}\ s^{-1}$. From the equilibrium constant $K = 5.5 \times 10^4$ M and the redox potential $E(Br_2^{\bullet-}/2Br^-) = 1.63$ V we calculate $E(N_3^\bullet/N_3^-) = 1.35 \pm 0.02$ V vs. NHE. Cyclic voltammetry experiments with N_3^- showed a single peak on the anodic scan and no peak on the cathodic scan due to the rapid decay of the N_3 radicals. From the dependence of peak potential on scan rate we derive $E_{1/2}$ for the $N_3^\bullet/N_3^-$ couple, 1.32 ± 0.03 V vs. NHE.

Introduction

The azidyl radical is one of the most important one-electron oxidants used in fast kinetic studies, particularly pulse radiolysis.[1-5] It is produced by the diffusion-controlled reaction of azide ions with hydroxyl radicals[6]

$$N_3^- + OH^\bullet \rightarrow N_3^\bullet + OH^- \qquad (1)$$

and it has been applied extensively for the one-electron oxidation of phenols, anilines, and many biologically important molecules.[1-5]

$$N_3^\bullet + PhOH \rightarrow N_3^- + PhO^\bullet + H^+ \qquad (2)$$

The rate constants for the oxidation of a wide variety of organic substrates with $N_3^\bullet$ [1-5] are generally higher than those with other

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radicals[7,8] and were taken to indicate that $N_3^\bullet$ is a very strong oxidant. This qualitative observation was supported by the first estimate[9] of the redox potential of the $N_3^\bullet/N_3^-$ couple, $E = 1.9$ V vs. NHE, derived from flash photolysis experiments with $Co(NH_3)_5N_3^{2+}$ in the presence of I^- and Br^-. The $N_3^\bullet$ radical produced by photolysis of the complex was found to oxidize I^- to produce $I_2^{\bullet-}$. On the other hand, in the presence of excess Br^- the $Br_2^{\bullet-}$ radical was not observed. Instead, another transient, suggested to be $BrN_3^{\bullet-}$, was formed. The authors concluded that $N_3^\bullet$ is a little poorer oxidant than Br and estimated $E(N_3^\bullet/N_3^-) = 1.9$ V.

A value of $E(N_3^\bullet/N_3^-) = 1.87$ V was also estimated[10] from the lowest observed CTTS (charge transfer to solvent) transition.[11] Later studies, however, discovered a lower energy CTTS band which suggests $E(N_3^\bullet/N_3^-) = 1.30$ V.[12]

The value of $E(N_3^\bullet/N_3^-)$ was calculated[13] more recently from the enthalpy of formation $N_3(g)$, deduced from the electron affinity of $N_3(g)$[13] and the proton affinity of N_3^-,[14] $\Delta H_f^\circ(N_3(g)) = 112$ kcal/mol. Estimating the hydration enthalpy and the entropy of N_3 from similar small molecules, the authors derived $E(N_3^\bullet/N_3^-) = 1.37$ V. However, the photochemical threshold for dissociation of NCN_3 to CN and N_3 radicals gives $\Delta H_f^\circ(N_3(g)) = 99$ kcal/mol,[16] which would lead to $E(N_3^\bullet/N_3^-) = 1.93$ V.

Kinetic studies of the reactions of N_3^- with Ir^{IV} and Fe^{III} complexes led to an estimate of $E(N_3^\bullet/N_3^-) = 1.56$ V.[13] Recent improvements in the same experiments,[17] achieved by the addition of a spin trap to capture the $N_3^\bullet$ radicals and prevent their back-reactions, indicated that a better value for $E(N_3^\bullet/N_3^-)$ is 1.33 V. This value is considerably lower than the redox potential for $Br_2^{\bullet-}/2Br^-$,[18-20] while the rate constants for oxidation by $N_3^\bullet$ are usually much higher than those for oxidation by $Br_2^{\bullet-}$. Because of all the inconsistencies mentioned above it appeared worthwhile to study the redox potential of the $N_3^\bullet/N_3^-$ couple by direct pulse radiolysis experiments with the halide and pseudohalide ions and radicals and also to attempt to measure it directly by cyclic voltammetry. Our results from both techniques are in good agreement with the latest value of 1.33 V reported by Ram and Stanbury.[17]

Experimental Section

All the compound used were analytical grade reagents of the highest purity commercially available. Water was purified by a Millipore Milli-Q system.[21] Solutions were prepared freshly before each experiment and were deoxygenated by bubbling with pure nitrous oxide. The N_2O serves also to scavenge the hydrated electrons and converts them to OH radicals. Pulse radiolysis experiments were carried out with the apparatus described previously.[22] Pulses of 2-MeV electrons from a Febetron were used to deliver doses of 3 to 10 Gy/pulse. The radicals were monitored at their absorption maxima: Br_2^-, 360 nm; I_2^-, 380 nm; $(SCN)_2^-$, 480 nm; N_3, 275 nm. Kinetic spectrophotometric traces were digitized with a Tektronix 7612 digitizer and rate constants calculated by a least-squares routine.

For cyclic voltammetry experiments, aqueous solutions of NaN_3 ($\sim$5 mM) containing Na_2SO_4 (0.2 M) and buffer (2 mM) were purged with N_2. The working electrode was a highly polished glassy carbon disk and a SCE reference was used together with a Pt counterelectrode. The working electrode was polished before each scan and many scans were averaged to obtain the peak potential (±20 mV). A Rank E611 potentiostat was driven by a purpose-built triangle wave generator. For each solution, the scan rate (ν) was varied from 0.015 to 0.550 V/s and both peak potential (E_p) and peak current (i_p) determined from the voltammograms.

Results and Discussion

The redox potentials of the pairs $X^\bullet/X^-$ and $X_2^{\bullet-}/2X^-$, where X = Br, I, and SCN, have been determined by several authors.[18-20,23,24] Using different methods they derived fairly consistent values. The most recent measurements gave $E(I_2^{\bullet-}/2I^-) = 1.03$ V, $E(I/I^-) = 1.33$ V, $E(Br_2^{\bullet-}/2Br^-) = 1.63$ V, $E(Br/Br^-) = 1.93$ V, $E((SCN)_2^{\bullet-}/2SCN^-) = 1.31$ V, and $E(SCN/SCN^-) = 1.62$ V. Since we expected $E(N_3^\bullet/N_3^-)$ to be within the same range of redox potentials, we examined the possible reactions of $N_3^\bullet$ or N_3^- with these halide and thiocyanate ions and radicals. The reactions were studied by pulse radiolysis of N_2O-saturated neutral aqueous solutions containing azide and one of the other anions.

The I^- + N_3^- System. In the pulse radiolysis of N_2O-saturated solutions of I^- the formation and decay of $I_2^{\bullet-}$ radicals were monitored at 380 nm. Addition of increasing concentrations of N_3^- resulted in a certain degree of competition for the OH radicals but had no effect on the rate of decay of $I_2^{\bullet-}$. From experiments with 0.2 M N_3^- we estimate an upper limit of $k < 5 \times 10^5$ M^{-1} s^{-1} for the reaction of $I_2^{\bullet-}$ with N_3^-. On the other hand, when I^- was added to solutions containing excess N_3^-, the characteristic absorption at 380 nm is observed. The rate of formation of this absorption increases linearly with $[I^-]$ and a second-order rate constants of $k_f = (4.5 \pm 1.2) \times 10^8$ M^{-1} s^{-1} is derived for the reaction

$$N_3^\bullet + I^- \rightleftarrows N_3^- + I^\bullet \tag{3}$$

This is followed very rapidly ($k_f = 1.2 \times 10^{10}$ M^{-1} s^{-1}, $K = 1.1 \times 10^5$ M^{-1})[24] by

$$I^\bullet + I^- \rightleftarrows I_2^{\bullet-} \tag{4}$$

so that the overall reaction is

$$N_3^\bullet + 2I^- \rightarrow N_3^- + I_2^{\bullet-} \tag{5}$$

The Br^- + N_3^- System. The formation and decay of the $Br_2^{\bullet-}$ radicals in the pulse radiolysis of Br^- solutions were monitored at 360 nm. Addition of azide to these solutions resulted in two effects. Competition for the OH radicals caused a decrease in the initial $Br_2^{\bullet-}$ concentration produced by the pulse and, furthermore, the decay of $Br_2^{\bullet-}$ became much faster in the presence of azide and followed first-order kinetics. The preliminary experiments indicated that $Br_2^{\bullet-}$ oxidizes N_3^- with a rate constant on the order of 10^8 M^{-1} s^{-1}. When the concentration of Br^- was raised above 1 M and that of N_3^- lowered below 1 mM it became clear that $Br_2^{\bullet-}$ does not decay to zero in the initial first-order process but that a plateau value remains which then decays more slowly by a second-order process. The plateau level and the kinetics leading to the plateau depend on the concentrations of both Br^- and N_3^- as expected for the equilibrium

$$Br_2^{\bullet-} + N_3^- \rightleftarrows 2Br^- + N_3^\bullet \tag{6}$$

The reaction of $Br_2^{\bullet-}$ with N_3^- was also suggested to lead to formation of a complex $BrN_3^{\bullet-}$ with a different absorption

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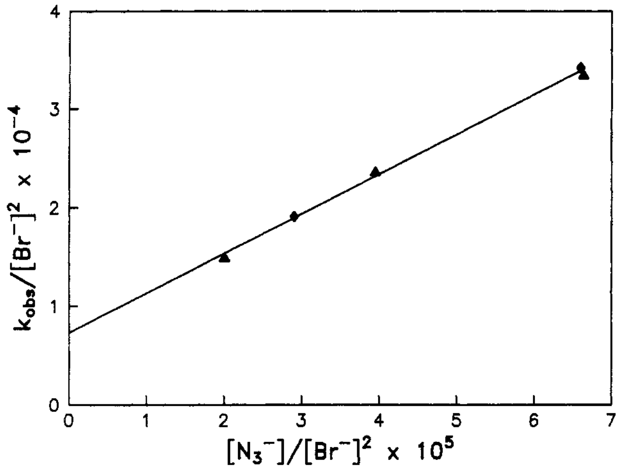

Figure 1. A plot of k_{obsd} for reaction 6 as a function of concentration ratios showing that the reaction goes to equilibrium. The absolute concentration of the Br^- was 3 (▲) or 2 M (◆).

spectrum. In our experiments we have examined the spectrum of the initially formed $Br_2^{\bullet-}$ radicals and the spectrum at the plateau level reached after reaction 6 and found them to be identical in the range of 320 to 470 nm. This suggests that reaction 6 goes to equilibrium as formulated and does not form other complexes. This is not surprising since complex formation between $N_3^\bullet$ radicals and N_3^- was shown to have a very low equilibrium constant.[2]

The equilibrium constant for reaction 6 can be calculated either from the concentrations at equilibrium according to

$$K_6 = \frac{[N_3^\bullet][Br^-]^2}{[Br_2^{\bullet-}][N_3^-]}$$

or from the kinetics leading to equilibrium: $K_6 = k_f/k_r$ and $k_{obsd} = k_f[N_3^-] + k_r[Br^-]^2$. A plot of $k_{obsd}/[Br^-]^2$ vs. $[N_3^-]/[Br^-]^2$ gives a straight line with a slope equal to k_f and an intercept equal to k_r. From the plot in Figure 1 we derive $k_f = 4.0 \times 10^8$ M^{-1} s^{-1} and $k_r = 7.3 \times 10^3$ M^{-2} s^{-1}. Thus the equilibrium constant is $K = 5.5 \times 10^4$ M, which yields $\Delta E = 280$ mV for the difference in redox potential between the bromide and the azide system. A similar equilibrium constant was calculated by using the plateau levels to derive the concentration ratio $[N_3^\bullet]/[Br_2^{\bullet-}]$ at equilibrium. The accuracy of the latter measurements was somewhat less satisfactory than that of the kinetic measurements because in many experiments a certain overlap between the first-order decay and the subsequent second-order decay masked the exact value of the plateau level. Nevertheless, all measurements fall within the range of $\Delta E = 280 \pm 15$ mV. From $E(Br_2^{\bullet-}/2Br^-) = 1.63$ V[20] we calculate $E(N_3^\bullet/N_3^-) = 1.35$ V.

The SCN^- + N_3^- System. From the above results with the Br^- system we find that the redox potential for $N_3^\bullet$ is very similar to that for $(SCN)_2^{\bullet-}$. Therefore, we attempted to observe the oxidation of N_3^- by $(SCN)_2^{\bullet-}$ and the oxidation of SCN^- by $N_3^\bullet$. Experiments with solutions containing both SCN^- and N_3^- showed that the initial absorption at 480 nm due to $(SCN)_2^{\bullet-}$ produced after the pulse reflects the competition between SCN^- and N_3^- for the OH radicals. The decay of this absorption did not appear to change upon addition of relatively low concentrations of azide. However, when both N_3^- and SCN^- were present at somewhat similar concentrations the decay at 480 nm became faster. This effect was independent of the absolute concentrations of either azide or thiocyanate ions but strongly dependent on their ratio, i.e. the increase in rate appeared only when a considerable portion of the OH radicals reacted with each ion. Under these conditions, the 480-nm absorption decayed in two successive steps. We ascribe the fast decay to reaction of $(SCN)_2^{\bullet-}$ with $N_3^\bullet$ and the slower decay to self-reaction of $(SCN)_2^{\bullet-}$ after the $N_3^\bullet$ was consumed. Thus no evidence for reaction between $(SCN)_2^{\bullet-}$ and N_3^- or between $N_3^\bullet$ and SCN^- is found within the lifetime of these radicals.

Cyclic Voltammetry. The above pulse radiolysis results give a reliable redox potential for the $N_3^\bullet/N_3^-$ couple which is in very good agreement with the recent value determined by Ram and Stanbury.[17] No attempt has been made to date to determine this redox potential by cyclic voltammetry. This technique is generally very reliable for reversible reactions only. Recently, however, we have utilized cyclic voltammetry to determine the redox potential of $SO_2^{\bullet-}$ which is a short-lived radical.[25] It appeared worthwhile to attempt a similar experiment with N_3^-.

Scanning between 0 and 1.6 V vs. NHE produced ~~a single~~ peak on the anodic scan. Even on the fastest scan rate, no peak could be resolved on the reverse cathodic scan. The peak current was a linear function of the square root of the voltage scan rate, showing that the electrode process is diffusion controlled. The peak potential varied with the voltage scan rate but was found to be independent of pH. For pH 11.1, 9.3, 7.0, 6.0, 4.7, and 3.1 the values of E_p were 1.26, 1.30, 1.28, 1.30, 1.29, and 1.32 V vs. NHE, respectively, at a scan rate of 0.06 V/s. The average E_p value is 1.29 ± 0.03 V.

Assuming that the electrode oxidation step is followed by a rapid chemical process according to

$$N_3^- \rightarrow N_3^\bullet + e^- \qquad (7)$$

$$2N_3^\bullet \rightarrow 3N_2 \qquad (8)$$

one can relate the E_p values to $E_{1/2}$ by the equation:[26]

$$E_p = E_{1/2} - 0.90(RT/nF) + (RT/3nF) \ln (2kC_0RT/3nF) \qquad (9)$$

where k is the bimolecular rate constant for the decay of the azidyl radical and C_0 is the initial concentration of the electrode active material. From plots of E_p vs. log ν, the average $E_{1/2}$ for azide ion is found to be 1.32 ± 0.03 V vs. NHE.

Conclusion

The value of $E(N_3^\bullet/N_3^-)$ measured by cyclic voltammetry is in very good agreement with that measured from the equilibrium with $Br_2^{\bullet-}$ and also with the redox potential reported recently by Ram and Stanbury.[17] We have to assume that the higher values estimated earlier were inaccurate.

The rate constants for oxidation by $N_3^\bullet$ radicals are in general much faster than those for oxidation by I_2^-, $(SCN)_2^-$, Br_2^-, and Cl_2^-. Substituent effects also show that $N_3^\bullet$ exhibits lower selectivity than the other radicals. Since the redox potential of $N_3^\bullet$ is considerably lower than those of Br_2^- and Cl_2^- we conclude that the higher rates of oxidation by $N_3^\bullet$ are due to a faster self-exchange rate for $N_3^\bullet/N_3^-$.

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Registry No. N_3^-, 14343-69-2; $N_3^\bullet$, 12596-60-0; I^-, 20461-54-5; $I_2^{\bullet-}$, 12190-71-5; Br^-, 24959-67-9; $Br_2^{\bullet-}$, 12595-70-9; $(SCN)_2^{\bullet-}$, 34504-17-1; SCN^-, 302-04-5.

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