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Redox Potentials of the Azide and Dithiocyanate Radicals

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We have measured the midpoint potentials of the two redox couples azidyl radical/azide and dithiocyanate radical anion/thiocyanate. The two-pulse radiolytically determined potentials were obtained with use of the same reference couple, tris(bipyridine)ruthenium(III)/tris(bipyridine)ruthenium(II), and by both kinetic and equilibrium protocols. On the basis of the equilibrium constants measured for the reactions between the inorganic radicals and the ruthenium complex, the calculated E_m' at 25 °C for azidyl radical/azide is 1.33 ± 0.01 V (NHE) and for dithiocyanate radical/thiocyanate, 1.29 ± 0.01 V (NHE). The observed kinetics for the one-electron oxidation of azide by the dibromide radical anion suggests that an intermediate monomeric neutral bromide radical species may be the actual oxidizing species.

Introduction

Since the azide radical, $N_3^{\bullet}$,[1] is a particularly useful one-electron oxidant of biologically significant aromatic compounds,[2] it is surprising that the reported values of the $N_3^{\bullet}/N_3^-$ redox potential vary between 1.30 and 1.93 V.[2b] The lowest estimate of ca. 1.30 V may be the best since it is now supported by three recent independent measurements,[3,6] but this low value appears inconsistent with the fact the $N_3^{\bullet}$ oxidizes a large number of compounds faster (e.g., ref 4) than does $Br_2^{\bullet -}$, acknowledged to have a redox potential of 1.63 V.[5] Moreover, these low estimates are theoretically uncertain because of the methods by which they were obtained.

Alfassi et al.[3] determined the $N_3^{\bullet}/N_3^-$ potential by two methods: (i) electrochemical oxidation as obtained by cyclic voltammetry and (ii) equilibration of $N_3^{\bullet}$ with the dibromide anion radical. Electrochemical oxidation of azide is irreversible because of rapid $N_3^{\bullet}$ decay. Thus, these authors' reported reversible E_m was obtained from the observed peak position of a cyclic voltammetric wave and a calculated correction based on the assumption that the radical's decay product is not electroactive.[7] In the $N_3^{\bullet}$-dibromide experiments, they measured the equilibrium kinetics of the pulse radiolytically initiated reaction:

$$Br_2^{\bullet -} + N_3^- \rightleftharpoons 2Br^- + N_3^{\bullet} \qquad (1)$$

From the dependence of the apparent rate constant, K_{app}, on N_3^- concentration, they used the following relationship to calculate an equilibrium constant.

$$k_{app} = k_f(N_3^-) + k_b(Br^-)^2 \qquad (2)$$

However, eq 2 assumes implicitly that (1) is an elementary reaction. This is an unlikely proposition, since the reoxidation of Br^- by $N_3^{\bullet}$ would then be termolecular. We shall show later that eq 2 is, in fact, not applicable to reaction 1. Our second reservation is their reported ΔE of 0.28 V between the $N_3^{\bullet}/N_3^-$ couple and the reference $Br_2^{\bullet -}/2Br^-$. In our experience, the determination of a redox potential may not be reliable when the ΔE between unknown and reference couples is larger than 0.10–0.15 V.[8]

Because of these concerns and because of our increasing dependence on the azide radical as a one-electron oxidant, we undertook a reevaluation of the $N_3^{\bullet}/N_3^-$ redox potential. Our approach was to determine both the equilibration kinetics *and* the equilibrium position of the pulse radiolytically initiated reaction:

$$Ru(bpy)_3^{2+} + N_3^{\bullet} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Ru(bpy)_3^{3+} + N_3^- \qquad (3)$$

Two advantages in the use of $Ru^{III}(bpy)_3/Ru^{II}(bpy)_3$ as a reference couple for $N_3^{\bullet}/N_3^-$ are (i) its reported redox potential of 1.27 V at pH 7,[9] close to the value of ca. 1.30 V proposed for $N_3^{\bullet}/N_3^-$, and (ii) the likelihood that (3) is an elementary reaction, a likelihood that can be tested by comparison of kinetic and equilibrium results. As we shall report here, we obtained a midpoint potential identical, subject to experimental error, with that reported by Alfassi et al.,[3] notwithstanding the theoretical and practical concerns that prompted this reevaluation.

The redox potential of the $(SCN)_2^{\bullet -}/2(SCN)^-$ couple is also uncertain. While initially reported to be 1.5 V,[10] Schwarz and Bielski[11a] calculated values of 1.29 and 1.33 V; these values were based on their measured $I_2^{\bullet -}/2I^-$ and $Br_2^{\bullet -}/2Br^-$ redox potentials coupled to $(SCN)_2^{\bullet -}/2(SCN)^-$ through a series of equilibria measured by Schöneshöffer and Henglein.[12] Stanbury and coworkers,[11b] using this same series of equilibria and their own estimated $I_2^{\bullet -}/2I^-$ redox potential, reported a value of 1.35 V for the $(SCN)_2^{\bullet -}/2(SCN)^-$ couple. Merényi et al.[13] obtained a value of 1.35 V using their measured tryptophan radical redox potential and the reported equilibrium constant for the $(SCN)_2^{\bullet -}$ oxidation of tryptophan.[14] Finally, Alfassi et al.[3] stated that they were unable to obtain the $(SCN)_2^{\bullet -}/2(SCN)^-$ redox potential. With its redox potential of 1.27 V, $Ru^{III}(bpy)_3/Ru^{II}(bpy)_3$ may also be applicable to the measurement of the $(SCN)_2^{\bullet -}/2(SCN)^-$ E_m' via the reaction equilibrium

$$Ru(bpy)_3^{2+} + (SCN)_2^{\bullet -} \rightleftharpoons Ru(bpy)_3^{3+} + 2(SCN)^- \qquad (4)$$

With this equilibrium reaction, one faces the same theoretical

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(1) The abbreviations used here are $Br_2^{\bullet -}$, the dibromide anion radical; $N_3^{\bullet}$, the azide radical; $Ru^{II}(bpy)_3$, tris(bipyridine)ruthenium(II); $(SCN)_2^{\bullet -}$, the dithiocyanate anion radical.

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(11) (a) Schwarz, H. A.; Bielski, B. H. J. *J. Phys. Chem.* **1986**, *90*, 1445–1448. (b) Stanbury, D. M.; Wilmarth, W. K.; Khalaf, S.; Po, H. N.; Byrd, J. E. *Inorg. Chem.* **1980**, *19*, 2715–2722. These authors actually reported the redox potential for the couple $SCN^{\bullet}/SCN^-$. We have calculated the redox potential for the dithiocyanate radical based on the reported equilibrium constant of 2 × 10^5 for the formation of the $(SCN)_2^{\bullet -}$ from SCN^- and $SCN^{\bullet}$.[20a]

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difficulty mentioned with reference to reaction 1; namely, the kinetic protocol is of limited use without an a priori knowledge of the reaction scheme. However, with the mechanism-independent equilibrium protocol, we did obtain the $(SCN)_2^{\bullet -}/2(SCN)^-$ redox potential, which turns out to be similar to that reported by Schwarz and Bielski.[11a] As we shall also show, the kinetic protocol based on the empirical use of an expression analogous to eq 2 yields the same $(SCN)_2^{\bullet -}/2(SCN)^-$ E_m'. Apparently, eq 2 and that for its thiocyanate cousin yield reliable equilibrium constants even though they cannot be correct theoretically. We shall suggest a resolution to this apparent contradiction.

Experimental Section

We initiated all pulse radiolysis experiments with a short (ca. 200 ns), high energy (ca. 4 MeV, from The Ohio State Varian linear accelerator[15]) electron pulse introduced into a 5 mM, pH 7.0, phosphate buffer that contained NaN_3 or KSCN and had been saturated with oxygen-free[16] N_2O. The initial radical concentrations, determined by the method of Fielden,[17] were always within the range of 0.9–1.5 μM, well below the concentrations of all the other reactants so as to ensure pseudo-first-order kinetics in the subsequent equilibration reactions. All reactions were monitored at convenient wavelengths with the incident light filtered to minimize potential photoinduced side reactions.

For the pulse radiolytic determination of the $Ru^{III}(bpy)_3$ minus $Ru^{II}(bpy)_3$ difference spectrum, the reaction solutions contained 0.1 M NaN_3 and 25 μM $Ru^{II}(bpy)_3$. Our procedure was to monitor the absorbance change due to $N_3^\bullet$ oxidation of $Ru^{II}(bpy)_3$ at one wavelength, replace the contents of the reaction cell with a fresh solution, change the wavelength, repeat the oxidation, etc. We then reconstructed difference spectra as a function of time from the individual kinetic absorbance traces obtained at the various wavelengths. We also measured a static difference spectrum by oxidizing 150 μM $Ru^{II}(bpy)_3$ with ca. 1 equiv of ammonium cerium(IV) sulfate dissolved in 0.8 M sulfuric acid. The resultant difference spectrum was recorded on a Kontron UV/vis spectrophotometer with a reference solution that contained all the components except the cerium salt.

In electrochemical experiments, we utilized a Princeton Applied Research (PAR, Princeton, NJ) Model 173D potentiostat/galvanostat and a Model 174A polarographic analyzer. The experiments were done in a Metrohm three-electrode glass cell (Brinkmann Instruments, Westbury, NY) with a glassy carbon working electrode of 0.2-cm^2 exposed area, a platinum counter electrode, and a calomel electrode as reference. The degassed solutions were similar to those of the pulse radiolysis experiments, except that argon replaced the N_2O and KCl replaced the salt that had served as the precursor for the inorganic radical.

We extracted first-order rate constants from absorbance versus time profiles with the nonlinear regression analysis provided in the data-acquisition package ASYST (Macmillan Software, New York, NY). All other linear and nonlinear data analysis was done with the commercial package MINSQ (Micromath, Salt Lake City, UT).

$Ru(bpy)_3Cl_2 \cdot 6H_2O$ was purchased from Strem (Newburyport, MA) and used without further purification. Sodium azide and potassium thiocyanate were of the highest quality commercially available. Water was purified by a Millipore Milli-Q apparatus.

Results

Before $Ru^{III}(bpy)_3/Ru^{II}(bpy)_3$ is used as a reference couple in the determinations of the $N_3^\bullet/N_3^-$ and $(SCN)_2^{\bullet -}/2(SCN)^-$ redox potentials, it is necessary to obtain an electrochemical estimate of this standard's redox potential under the conditions of the pulse radiolysis studies to follow. As seen in Figure 1, $Ru^{II}(bpy)_3$ undergoes a one-electron, reversible oxidation in both cyclic voltammetric and differential pulse polarographic measurements. From these types of determinations, we obtained an E_m' of 1.28 ± 0.01 V (vs NHE), which is close to the reported $E^{\circ\prime}$ of 1.27 V.[9]

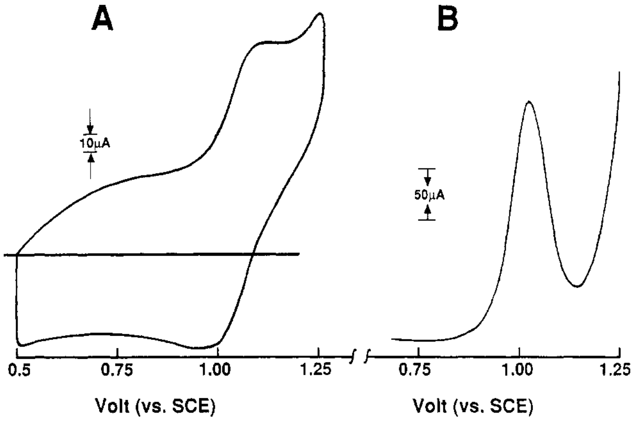

Figure 1. Electrochemistry of $Ru^{II}(bpy)_3$. (A) Cyclic voltammetry. (All concentrations as in B. Sweep rate was 200 mV/s. The increase in current between 0.5 and 0.75 V is due to surface carbon oxidation.) (B) Differential pulse polarography. (The concentrations of $Ru^{II}(bpy)_3$, KCl, and phosphate, pH 7.0, were 0.001, 0.1, and 0.005 M, respectively, with the solution saturated by argon. The scan rate was 2 mV/s.)

The primary radicals of aqueous pulse radiolysis were converted to the one-electron oxidant $N_3^\bullet$ via the common reactions

$$e_{aq}^- + N_2O \xrightarrow{H_2O} N_2 + OH^\bullet + OH^-$$

$$OH^\bullet + N_3^- \rightarrow OH^- + N_3^\bullet \qquad (5)$$

By keeping the azide to $Ru^{II}(bpy)_3$ concentration sufficiently large, we avoided the competitive formation of the $OH^\bullet$ adduct:[18]

$$OH^\bullet + Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+}\text{–}OH \qquad (6)$$

The absence of changes at 740 nm, where the hydroxyl adduct absorbs, assured us that reaction 6 had not occurred. The $Ru^{III}(bpy) - Ru^{II}(bpy)$ difference spectrum obtained with reactions 5 and 3 was qualitatively the same as the difference spectrum obtained in the Ce(IV) oxidation of $Ru^{II}(bpy)$ (Figure 2). We were, however, unable to oxidize the metal complex stoichiometrically with $N_3^\bullet$; this complex absorbs so intensely in both oxidation states that it was impossible to raise the $Ru^{II}(bpy)_3$ concentration sufficiently high enough to trap all the $N_3^\bullet$ before its rapid decay. Nonetheless, comparison of the two spectra indicates clearly the one-electron oxidation of $Ru^{II}(bpy)_3$ by $N_3^\bullet$ in the pulse radiolysis experiments. It is also important to note here that $Ru^{II}(bpy)_3$ is stable in aqueous solution for greater than 1 day, while the oxidized species must be stable for at least milliseconds, long enough for our experiments.

There is both a kinetic and an equilibrium method with which to determine the equilibrium constant for the oxidation of a reference compound by the azide radical:

$$N_3^\bullet + R \underset{k_b}{\overset{k_f}{\rightleftharpoons}} N_3^- + R^+ \qquad (7)$$

where R stands for the reference, in this case the ruthenium complex. We present our data for the kinetic protocol first.

If the concentrations of R and N_3^- are significantly larger than that of the azide radical and if reaction 7 is elementary (single step), then the equilibration will be first order with an apparent rate constant

$$k_{app} = k_f(R) + k_b(N_3^-)$$

$$(N_3^\bullet) \ll (N_3^-),(R) \qquad (8)$$

Hence, a plot of k_{app} versus a variable $Ru^{II}(bpy)_3$ concentration

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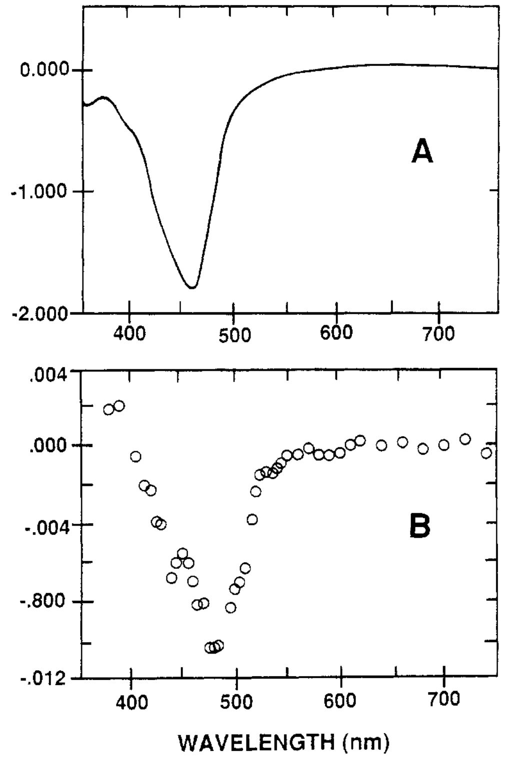

Figure 2. $Ru^{III}(bpy)_3 - Ru^{II}(bpy)_3$ difference spectra: (A) UV-visible absorption difference spectrum obtained as described in the Experimental Section; (B) plot constructed from pulse radiolysis time profiles obtained at individual wavelengths with identical results obtained at 0.2 and 1.8 ms after the pulse (The concentrations of $Ru^{II}(bpy)$, NaN_3, and phosphate, pH 7.0, were 25 μM, 0.1 M, and 5 mM, respectively. The initial concentration of the azide radical that served as the ruthenium complex oxidant was 2 μM. Spectrophotometer slit width 6.6 nm.)

at a constant N_3^- concentration should be a straight line (Figure 3) with slope k_f and intercept $k_b(N_3^-)$. The reaction equilibrium constant is then calculated from the ratio of k_f/k_b, which is *slope* × *(N₃⁻)/intercept*, and the $N_3^\bullet/N_3^-$ midpoint potential is obtained with the known E_m' of the reference couple and the two equations

$$\Delta E' = 0.0591 \log [K_{eq}] \tag{9}$$

$$E'_{N_3^\bullet/N_3^-} = \Delta E' + E'_{R^+/R} \tag{10}$$

where the prime indicates pH 7.0. Because of our concerns over possible interference by the competing insertion reaction (6), we carried out this kinetic analysis at more than one azide concentration. There was no dependence of the measured $\Delta E'$ on azide concentration, and the E_m' for $N_3^\bullet/N_3^-$, averaged over all our experiments, is 1.34 ± 0.02 V vs NHE.

We also obtained the $N_3^\bullet/N_3^-$ midpoint potential with an equilibrium protocol. For reaction 7, the visible absorbances A_0, at time zero, and A_{eq}, at equilibrium, are given (if the light path is 1 cm long) by

$$A_0 = \epsilon_R(R)_0 + \epsilon_{N_3^-}(N_3^-)_0 + \epsilon_{R^+}(R^+)_0 + \epsilon_{N_3^\bullet}(N_3^\bullet)_0$$

$$A_{eq} = \epsilon_R(R)_{eq} + \epsilon_{N_3^-}(N_3^-)_{eq} + \epsilon_{R^+}(R^+)_{eq} + \epsilon_{N_3^\bullet}(N_3^\bullet)_{eq} \tag{11}$$

where ϵ refers to the appropriate extinction coefficient, and R and R^+ can be $Ru^{II}(bpy)_3$ and $Ru^{III}(bpy)_3$, respectively. The set of independent equations required for a solution is completed with the inclusion of eqs 12 and 13, the equilibrium expression and the mass balance requirements, respectively. In our experiments, we measured absorbance changes between 480 and 500 nm where only $Ru^{II}(bpy)_3$ and $Ru^{III}(bpy)_3$ absorb; the concentrations of N_3^- and $Ru^{III}(bpy)_3$ were much greater than that of $N_3^\bullet$, and therefore, $(R)_0 \approx (R)_{eq}$ and $(N_3^-)_0 \approx (N_3^-)_{eq}$. Thus, eqs 11–13 can be simplified to

$$K_{eq} = \frac{(R^+)_{eq}(N_3^-)_{eq}}{(R)_{eq}(N_3^\bullet)_{eq}} \tag{12}$$

$$(R)_0 = (R)_{eq} + (R^+)_{eq}$$

$$(N_3^-)_0 = (N_3^-)_{eq} + (N_3^\bullet)_{eq}$$

$$(N_3^\bullet)_0 = (N_3^\bullet)_{eq} + (R^+)_{eq} \tag{13}$$

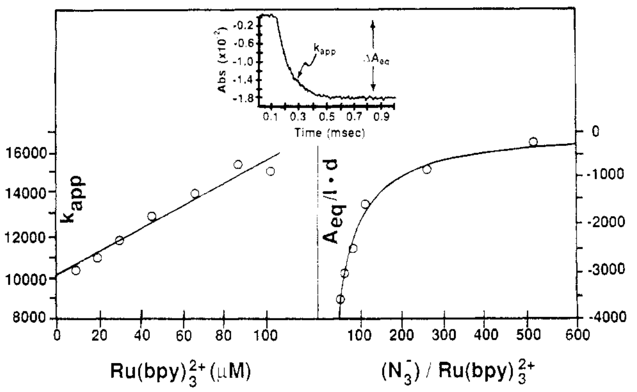

Figure 3. Determination of $N_3^\bullet/N_3^-$ redox potential by both kinetic and equilibrium pulse radiolysis protocols: (inset) time profile of an equilibration between $N_3^\bullet$ and $Ru(bpy)_3^{2+}$ (The concentrations of NaN_3, $Ru(bpy)_3^{2+}$, and phosphate, pH 7.0, were 5 mM, 65 μM, and 5 mM, respectively. The solution was saturated with N_2O at 25 °C, the initial $N_3^\bullet$ concentration was 1 μM, and the wavelength was set at 500 nm.); (left) plot of pseudo-first-order k_{app} versus $Ru(bpy)_3^{2+}$ concentration (The conditions were identical with those for the inset, except that the $Ru(bpy)_3^{2+}$ concentration was varied.); (right) plot of equilibrium absorbance data (The conditions were those for the results on the left. The solid line is the nonlinear least-squares fit of eq 14 in the text to the measured equilibrium absorbances.).

$$A_{eq} - A_0 = \frac{K_{eq}(\epsilon_{R^+} - \epsilon_R)}{K_{eq} + (N_3^-)_0/(R)_0} \tag{14}$$

The apparent $A_{eq} - A_0$ we obtained on varying the concentration ratio of azide/$Ru^{II}(bpy)_3$ are shown in Figure 3 together with a least-squares nonlinear fit of the data to eq 14. For this fit, the $N_3^\bullet/N_3^-$ E_m' was 1.32 ± 0.01 V, identical within experimental error with the kinetic protocol value. We conclude that the assumption of an elementary reaction (3), as required for the kinetic analysis, is valid. The unweighted average obtained from the combination of all kinetic and equilibrium data yields a $N_3^\bullet/N_3^-$ E_m' of 1.33 ± 0.01 V vs NHE.

With the same pulse radiolysis equilibrium protocol, we were also able to obtain K_{eq} for reaction 4, the dithiocyanate radical anion one-electron oxidation of $Ru(bpy)_3^{2+}$. As before, we measured $A_{eq} - A_0$ in the visible region, where, however, $(SCN_2^{\bullet -}$ absorbs strongly (ϵ_{472} = 7580 M^{-1} cm^{-1}).[19] Thus, eq 14 must be replaced by

$$A_{eq} - A_0 = \frac{K_{eq}(\epsilon_{R^+} - \epsilon_R) + (SCN^-)_0^2/(R)_0\epsilon_{(SCN)_2^{\bullet -}}}{K_{eq} + (SCN^-)_0^2/(R)_0} \tag{15}$$

In the inset of Figure 4 is a typical absorbance time profile obtained at 500 nm for the equilibrium reaction 4. The initial absorbance increase due to the rapid $OH^\bullet$ oxidation of thiocyanate to $(SCN)_2^{\bullet -}$ is followed by the first-order absorbance bleaching that accompanies both the one-electron reduction of $(SCN)_2^{\bullet -}$ to SCN^- and the oxidation of $Ru^{II}(bpy)_3$. The nonlinear fit of $A_{eq} - A_0$, the net absorbance changes in this series of reactions, to eq 15 (Figure 4, right panel) yields a K_{eq} of 1.69 ± 0.30 and a resultant $(SCN)_2^{\bullet -}/2(SCN)^-$ E_m' of 1.29 ± 0.01 V vs NHE at 25 °C. In Figure 4, we also show an apparently linear correlation between the pseudo-first-order equilibration rate constant, k_{app}, and the ruthenium complex concentration. We shall discuss the calculation of E_m' based on this linear dependence in the next section.

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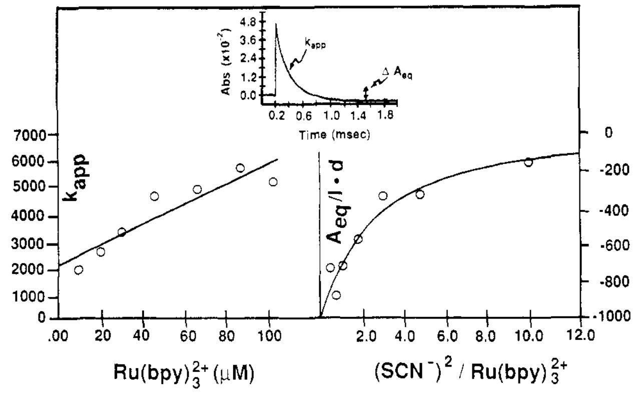

Figure 4. Determination of $(SCN)_2^{\bullet -}/2(SCN)^-$ redox potential by both kinetic and equilibrium pulse radiolysis protocols: (inset) time profile of one equilibration reaction between SCN^- and $Ru(bpy)_3^{2+}$ (The concentrations of KSCN, $Ru(bpy)_3^{2+}$, and phosphate, pH 7.0, were 0.01 M, 45 μM, and 5 mM, respectively. The solution was saturated with N_2O at 25 °C, the initial $(SCN)_2^{\bullet -}$ concentration was 1 μM, and the wavelength was set at 500 nm.); (left) plot of pseudo-first-order k_{app} versus $Ru(bpy)_3^{2+}$ concentration (The conditions were identical with those for the inset, except that the $Ru(bpy)_3^{2+}$ concentration was varied.); (right) plot of equilibrium absorbance data (The conditions were those for the results on the left. The solid line is the nonlinear least-squares fit of eq 15 in the text to the measured equilibrium absorbances.).

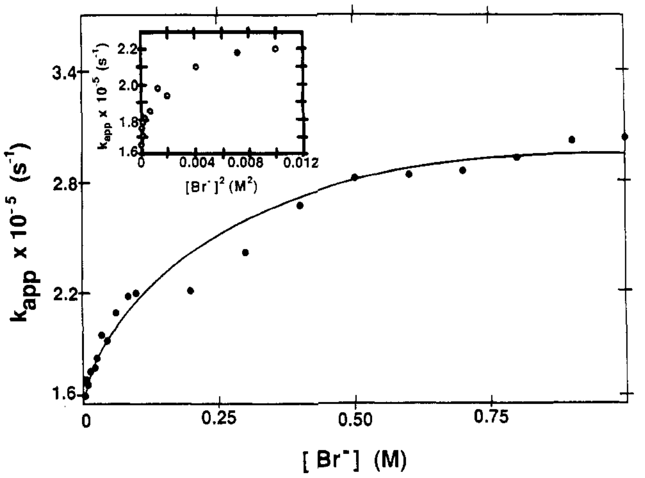

Figure 5. $N_3^\bullet/N_3^- - (Br_2)^{\bullet -}/2(Br)^-$ equilibration reaction: dependence on Br^- concentration. The experimental rate constants were determined as described in the text. The concentrations of all species were N_3^-, 1.0 mM; Br^-, 1.0 mM–1.0 M; phosphate buffer, 0.005 M, pH 7; initial radical concentration, ca. 1 μM. The solid line was obtained as the best fit of the data points to the equation $2k_{app} = a_0 + a_1(Br^-) - [a_2 + a_3(Br^-) + a_4(Br^-)^2]^{1/2}$. This equation is based on eq 20 of the text and the assignment of the fitting constants are $a_0 = k_1 + k_2(N_3^-)$; $a_1 = l_1 + l_2$; $a_2 = [k_2(N_3^-) - k_1]^2$; $a_3 = 2[k_2(N_3^-)(l_1 + l_2) + k_1(l_1 - l_2)]$; and $a_4 = (l_1 - l_2)^2$. (inset) Dependence of the apparent rate constant, k_{app}, on the square of the bromide concentration. The nonlinear dependence proves that eq 2 is invalid.

Discussion

We have measured redox potentials for both the $N_3^\bullet/N_3^-$ and $(SCN)_2^{\bullet -}/2(SCN)^-$ couples. For the $N_3^\bullet/N_3^-$ couple, we obtained 1.32 ± 0.01 V and 1.34 ± 0.02 V with the equilibrium and kinetic protocols, respectively. These values of E_m' are the same within experimental error, and so we report the unweighted average, 1.33 ± 0.01 V (NHE), of all individual data points as our best estimate for the $N_3^\bullet/N_3^-$ E_m'. This result is the same as the two potentials reported by Alfassi et al.—1.35 ± 0.02 V with the pulse radiolysis kinetic procedure and 1.32 ± 0.03 V from cyclic voltammetric measurements.[3] In spite of the concerns we enumerated in the introduction, our values agree with theirs. Are these concerns, thus, unfounded? In the case of the cyclic voltammetry, either the required assumption that $N_3^\bullet$ decays rapidly to a nonelectroactive product could be valid or any error introduced because the assumption is incorrect could be negligible. On the other hand, the assumption of eq 2 for the kinetic analysis of the pulse-radiolysis-initiated azide/bromide reaction of eq 1 must be incorrect. For while this equation predicts that k_{app} is proportional to the square of the azide concentration, the data we collected to test this prediction show clearly that there is no such dependence (Figure 5, inset). But, in spite of this theoretical shortcoming, Alfassi et al. appear to have calculated the correct $N_3^\bullet/N_3^-$ E_m' with eq 2. We shall return to this dilemma after considering the thiocyanate results.

The use of an equilibrium protocol to determine the $(SCN)_2^{\bullet -}/2(SCN)^-$ E_m' avoids reaction mechanism uncertainties. With the measured K_{eq} for reaction 4, we calculated an E_m' for this couple of 1.29 ± 0.01 V vs NHE, within experimental error the same as the potential of 1.31 V calculated by Schwarz and Bielski[11a] and slightly lower than the 1.35 V of Merényi et al.[13] The measurements of Merényi and co-workers were referenced to the tryptophan radical with their estimated redox potential of 1.08 V. After that potential is replaced with our own more recently measured value of 1.05 V,[8] their $(SCN)_2^{\bullet -}/2(SCN)^-$ E_m' becomes 1.32 V, similar to that of Schwarz and Bielski. We conclude that the midpoint potential of the dithiocyanate radical does lie between 1.29 and 1.32 V.

Realizing that dithiocyanate and dibromide radical reactions suffer from the same mechanistic uncertainties, we nonetheless fit the available (e.g., Figure 4—inset) $Ru(bpy)_3^{2+}$ concentration-dependent k_{app} of reaction 4 to eq 16. Use of this equation

$$k_{app} = k_f(Ru(bpy)_3^{2+}) + k_b(SCN^-)^2 \qquad (16)$$

assumes, as did Alfassi et al. for the azide–dibromide radical reaction, that the equilibration (4) is a single-step reaction. The plot of k_{app} versus $Ru(bpy)_3^{2+}$ is linear; from the value of *slope* × $(SCN^-)^2$/*intercept* taken from that plot, we calculated an equilibrium constant of 1.77 ± 0.48 and an E_m' of 1.29 ± 0.01 V, values identical within experimental error with those obtained with the equilibrium protocol. But, while this identity would suggest an elementary bimolecular reaction between $Ru(bpy)_3^{2+}$ and $(SCN^-)^2$, this cannot be the case; for, as argued previously in the $Br_2^{\bullet -}/N_3^-$ case, an elementary forward reaction implies by the principle of microscopic reversibility an elementary termolecular back-reaction of SCN^- oxidation by $Ru(bpy)_3^{3+}$, an unlikely proposition.

Hence, there is an interesting similarity between reactions 1 and 4. Both dihalide (pseudodihalide) radical oxidations appear to be single-step reactions in the sense that eq 2 and 16 yield E_m' experimentally identical with the E_m' obtained by eqs 14 and 15, respectively. But in both cases, oxidation is unlikely to be single step because of microscopic reversiblity. Moreover, eq 2 does not apply to the oxidation of azide by the dibromide radical anion, since that equation does not correctly describe the dependence of k_{app} on the bromide concentration (Figure 5, inset). We conclude, therefore, that the reaction of eq 1 must occur in two or more elementary steps and that by analogy this will be also true for the reaction of eq 4. The remainder of this discussion explores possible mechanisms for the two reactions.

The following is a two-step scheme that might apply to both $Br_2^{\bullet -}$ and $(SCN)_2^{\bullet -}$ reactions.

$$X_2^{\bullet -} \xrightleftharpoons[l_1]{k_1} X^- + X^\bullet$$

$$X^\bullet + R \xrightleftharpoons[l_2]{k_2} X^- + R^+ \qquad (17)$$

$$X = Br, SCN \qquad R = N_3^-, Ru^{II}(bpy)_3$$

Under two conditions, the scheme of eq 17 is consistent with our observed results. The first of these is the rapid preequilibrium condition; with both X^- and R present in excess over $X^\bullet$, the initial dimer dissociation is in equilibrium throughout the net reaction. This is a reasonable assumption, since the equilibrium constants for the dissociation of $(SCN)_2^{\bullet -}$ (Mamou et al., note 5) and $Br_2^{\bullet -}$[20]

are 5×10^{-6} and 4.5×10^{-6}, respectively. The apparent rate constant for the net reaction then becomes

$$k_{\mathrm{app}} = \frac{k_2K(\mathrm{R})}{(\mathrm{X}^-) + K} + l_2(\mathrm{X}^-) \qquad K = k_1/l_1 \tag{18}$$

Equation 18, in which k_{app} is not proportional to $(\mathrm{X}^-)^2$, predicts that a plot of k_{app} versus the concentration of R ($\mathrm{N_3^-}$ or $\mathrm{Ru^{II}(bpy)_3}$) at a fixed $\mathrm{X^-}$ (thiocyanate or bromide) concentration will be linear with a slope and intercept such that when $(\mathrm{X}^-) \gg K$

$$\frac{\text{slope}}{\text{intercept}}(\mathrm{X}^-)^2 \approx \frac{k_2}{l_2}K = K_{\mathrm{eq}}$$

Thus, scheme 17 yields eq 18, which is similar to (2) and (16) in that (i) (18) is linear with respect to the concentration of R ($\mathrm{N_3^-}$ and $\mathrm{Ru(bpy)_3^{2+}}$, respectively) and (ii) one would compute the same K_{eq} whether obtained by kinetic or equilibrium protocol.[21]

We can also derive an expression for k_{app} under the second condition, namely, that the concentrations of azide and bromide, $(\mathrm{N_3^-})$ and $(\mathrm{Br^-})$, are much greater than that of $(\mathrm{Br_2^{\bullet-}})_0$, the initial dihalide radical concentration. To obtain the integrated rate expression that will yield k_{app}, we begin with two rate equations and one mass balance relationship:

$$\mathrm{d}(\mathrm{Br_2^{\bullet-}})/\mathrm{d}t = -k_1(\mathrm{Br_2^{\bullet-}}) + l_1(\mathrm{Br^-})_0(\mathrm{Br^\bullet})$$

$$\mathrm{d}(\mathrm{N_3^\bullet})/\mathrm{d}t = k_2(\mathrm{Br^\bullet})(\mathrm{N_3^-})_0 - l_2(\mathrm{Br^-})_0(\mathrm{N_3^\bullet})$$

$$(\mathrm{Br_2^{\bullet-}}) + (\mathrm{N_3^\bullet}) + (\mathrm{Br^\bullet}) = (\mathrm{Br_2^{\bullet-}})_0 \tag{19}$$

Solving this system of three equations with the aid of Laplace–Carson transforms,[22] one obtains the integrated form of the rate equation for azide radical production.

$$(\mathrm{N_3^\bullet}) = k_1k_2(\mathrm{N_3^-})_0(\mathrm{Br_2^{\bullet-}})_0\left[\frac{1}{k_{\mathrm{app},1}k_{\mathrm{app},2}} - \frac{\exp[-k_{\mathrm{app},1}t]}{k_{\mathrm{app},1}(k_{\mathrm{app},2} - k_{\mathrm{app},1})} + \frac{\exp[-k_{\mathrm{app},2}t]}{k_{\mathrm{app},2}(k_{\mathrm{app},2} - k_{\mathrm{app},1})}\right]$$

$$2k_{\mathrm{app},i} = k_1 + k_2(\mathrm{N_3^-})_0 + (l_1 + l_2)\,(\mathrm{Br^-})_0 \pm [[k_1 + k_2(\mathrm{N_3^-})_0 + (l_1 + l_2)(\mathrm{Br^-})_0]^2 - 4k_1[k_2(\mathrm{N_3^-})_0 + l_2(\mathrm{Br^-})_0] - 4l_1l_2(\mathrm{Br^-})_0^2]^{1/2} \tag{20}$$

We have measured k_{app} for this reaction over a 1000-fold bromide concentration range and find a good fit of the experimental k_{app} to the negative root of (20) (Figure 5). (We chose the negative root, since it is reducible to the rapid equilibrium case.) Thus, scheme 17 is also consistent with the observed results by this criterion.

But, consistency is not proof of validity, and in scheme 17, it is $\mathrm{X^\bullet}$ and not $\mathrm{X_2^{\bullet-}}$ that is the oxidant of R. This is a proposal that may at first appear troublesome. Therefore, we shall consider whether there are other consistent and comparably simple schemes, and in particular two possible paths for the direct oxidation of R to $\mathrm{R^+}$ by the radical dimer $\mathrm{X_2^{\bullet-}}$. In the first, electron transfer and dithiocyanate or dibromide collapse occur simultaneously.

$$\mathrm{X_2^{\bullet-} + R \rightarrow 2X^- + R^+} \tag{21}$$

But, by the principle of microscopic reversibility, eq 21 is equivalent to the proposition that reaction 4 is elementary, a proposition we have already refuted experimentally for the reaction of azide with the dibromide radical anion. Hence, reaction scheme 21 is improbable. In the second, there is the formation of the intermediate dibromide species:

$$\mathrm{X_2^{\bullet-} + R \underset{l_1}{\overset{k_1}{\rightleftharpoons}} X_2^{2-} + R^+}$$

$$\mathrm{X_2^{2-} \leftrightharpoons 2X^-} \tag{22}$$

This scheme is also highly unlikely. First, because of microscopic reversibility, the reverse reaction, oxidation of $\mathrm{X^-}$ by $\mathrm{R^+}$, must occur via the dimerization:

$$\mathrm{2X^- \rightarrow X_2^{2-}}$$

which reaction would be followed by oxidation of $\mathrm{X_2^{2-}}$ to $\mathrm{X_2^{\bullet-}}$. That two negative halogen ions would dimerize under the conditions of our experiments is untenable. Second, it would be reasonable to propose that the functionally irreversible dissociation of $\mathrm{X_2^{2-}}$ to $\mathrm{X^-}$ would be so much faster than $\mathrm{X_2^{2-}}$ formation from $\mathrm{X_2^{\bullet-}}$ that the electron-transfer step would be rate-determining and, hence, the concentration of $\mathrm{X_2^{2-}}$ would be close to zero throughout the reaction. In this case, the rate of the back-reaction to $\mathrm{X_2^{\bullet-}}$ would then be close to zero, and

$$\mathrm{d}(\mathrm{R^+})/\mathrm{d}t = k_1(\mathrm{R})_0(\mathrm{X_2^{\bullet-}}) - l_1(\mathrm{X_2^{2-}})(\mathrm{R^+}) \approx k_1(\mathrm{R})_0(\mathrm{X_2^{\bullet-}})$$

But, this implies that the overall reaction would be independent of the halide concentration; this is certainly not true for the reaction between $\mathrm{N_3^\bullet}$ and $\mathrm{Br_2^{\bullet-}}$. In a less reasonable variant of scheme 22, one might assume a finite concentration of $\mathrm{X_2^{2-}}$ in equilibrium with $\mathrm{X^-}$. But, then it can be shown that while the resultant rate law would be pseudo-first-order, the dependence of k_{app} on the halide concentration would be that of eq 2; this is inconsistent with the observed bromide concentration dependence for the reaction between $\mathrm{N_3^\bullet}$ and $\mathrm{Br_2^{\bullet-}}$. Hence, reaction scheme 22 is eliminated as a possibility.

There may be more complex reaction schemes that are also consistent with our observations. We suggest, however, that reaction scheme 17 is a reasonable model and in the absence of additional experimental results it could be the mechanism for the one-electron oxidation of inorganic compounds by the dibromide radical anion in particular and of all dihalide (pseudodihalide) radicals in general. Two further conclusions can be drawn on the basis of this suggestion. First, while Alfassi et al. were not justified in using eq 2, they did fortunately obtain the correct $\mathrm{N_3^\bullet/N_3^-}$ potential. Second, on the basis of scheme 17, the dihalide or pseudodihalide radical anions would be expected to be kinetically less reactive oxidants than the azide radical, even though they possess the higher redox potentials. For as seen in the two eqs 18 and 20 derived on the basis of reaction scheme 17, the apparent oxidation rate constant contains a "correction" for the equilibrium between the di- and monohalide radical species. This equilibrium lies far to the side of the dimer in the case of bromide and thiocyanate, while the azide radical dimer is found only at very high azide concentrations. Hence, the azide radical appears more reactive because (i) it is a monomer in conditions in which the other halide and pseudohalide radicals are overwhelmingly dimeric and (ii) the monomeric radical species is the primary oxidant.

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Registry No. $\mathrm{N_3^\bullet}$, 12596-60-0; $\mathrm{N_3^-}$, 14343-69-2; $\mathrm{(SCN)_2^{\bullet-}}$, 34504-17-1; $\mathrm{SCN^-}$, 302-04-5; $\mathrm{Ru^{II}(bpy)_3^{2+}}$, 15158-62-0; $\mathrm{Ru^{III}(bpy)_3^{3+}}$, 18955-01-6; $\mathrm{Br_2^{\bullet-}}$, 12595-70-9; $\mathrm{Br_2}$, 7726-95-6; $\mathrm{Br^-}$, 24959-67-9.

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(20) (a) Baxendale, J. H.; Bevan, P. L. T.; Stott, D. A. *Trans. Faraday Soc.* **1968**, *64*, 2389–2397. (b) Behar, D.; Bevan, P. L. T.; Scholes, G. *J. Phys. Chem.* **1972**, *76*, 1537–1542. These authors reported the rate constants for formation and the breakdown of $\mathrm{(SCN)_2^{\bullet-}}$ as 6.8×10^9 $\mathrm{M^{-1}\,s^{-1}}$ and 3.4×10^4 $\mathrm{s^{-1}}$, respectively. (c) While Schñeshöffer and Henglein[12] did not report an equilibrium constant for this reaction, one can calculate a value of 1.9×10^5 from the data they do present.

(21) (a) When $\mathrm{X^-}$ is thiocyanate, the ratio k_2/l_2 from scheme 17 is 3.7×10^5, as calculated from our measured K_{eq} of 1.69 and the literature value for $K_{\mathrm{assoc}} = l_1/k_1$ of 2×10^5. The ΔE^7 for the single–step oxidation of $\mathrm{Ru^{II}(bpy)_3}$ by $\mathrm{SCN^\bullet}$ is thus 0.33 V. Since the $\mathrm{Ru^{II}(bpy)_3/Ru^{III}(bpy)_3}$ E_{m}' is 1.28 V, the estimated $\mathrm{SCN^\bullet/SCN^-}$ E_{m}' becomes 1.61 V, close to the value calculated by Schwarz and Bielski.[11a] (b) When the back-reaction of the first step in scheme 17 is faster than the forward reaction of the second step, then an initial equilibrium is assured. These rates can be estimated from the apparent k_{f} and k_{b} of 7×10^{10} and 2×10^5 $\mathrm{M^{-1}\,s^{-1}}$, respectively, taken from the slope and intercept of the straight line in Figure 4. Baxendale and co-workers[20a] proposed that the rate constant $l_1 = 7.6 \times 10^9$ $\mathrm{M^{-1}\,s^{-1}}$. From eq 18 and the ratio of k_2/l_2 computed above, $k_2 = 6.8 \times 10^{10}$ $\mathrm{M^{-1}\,s^{-1}}$. Under our reaction conditions, the thiocyanate concentration was always >10-fold the $\mathrm{Ru^{II}(bpy)_3}$ concentration. Hence, $l_1/k_2 > 1$, consistent with an initial fast equilibrium. On the other hand, a modified scheme 17 in which the initial dissociation is slow and the subsequent electron transfer fast yields an expression for k_{app} that is inconsistent with the experimental data.

(22) Rodiguin, N. M.; Rodiguina, E. N. *Consecutive Chemical Reactions: Mathematical Analysis and Development.* Van Nostrand: Princeton, NJ, 1964.