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Reactions Involving the Hydrazinium Free Radical: Oxidation of Hydrazine by Hexachloroiridate

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The oxidation of N_2H_4 by $IrCl_6^{2-}$ to form N_2 and $IrCl_6^{3-}$ has been studied in aqueous solution at 25.0 °C and at an ionic strength of 0.2 M (NaCl). Over the range from pH 1 to pH 10, with excess hydrazine, the rate law is $-d[IrCl_6^{2-}]/dt = k'[IrCl_6^{2-}][N_2H_4]_{tot}/(1 + [H^+]/K_a)$, where K_a is the acid ionization quotient of $N_2H_5^+$ ($K_a = 1.1 \times 10^{-8}$ M) and $k'/4$ (=5.0 × 10^3 M^{-1} s^{-1}) is the bimolecular rate constant for outer-sphere oxidation of N_2H_4 to $N_2H_4^+$. A pulse radiolysis study failed to detect reaction between $N_2H_4^+$ and $Fe(CN)_6^{4-}$, thus implying an upper limit to the rate constant of 3 × 10^6 M^{-1} s^{-1}. An estimate of an upper limit of $E°$ for the $N_2H_4^+/N_2H_4$ couple ($E° \leq 0.73$ V) indicates that there is a significant kinetic barrier to electron transfer, which is consistent with major geometry changes attendant on oxidation of N_2H_4.

Our continuing interest in the redox chemistry of small molecules has focused on transformations involving transfer of a single electron to generate simple free radicals. In an effort to maintain simplicity, the redox partners have been selected to be substitution inert, and so the reactions have all been outer-sphere. The studies have evolved from simple redox couples such as $I^-/I\cdot$ and $SCN^-/SCN\cdot$ having no substantial change in geometry,[1] through the O_2/O_2^- couple, which undergoes substantial reorganization,[2] to bent triatomics such as ClO_2/ClO_2^-, which must be described in terms of both bending and stretching.[3] In the current study, the $N_2H_4/N_2H_4^+$ couple incorporates a variety of modes in three dimensions and, perhaps, strong hydrogen-bonding effects.

There are several pertinent studies of the oxidation of N_2H_4 by substitution-inert complexes. Of particular note is the series of oxidations by $Mo(CN)_8^{3-}$, $W(CN)_8^{3-}$, and $Fe(CN)_6^{3-}$,[4] the latter also having been studied several times previously.[5] In these reactions the rate law requires that N_2H_4 rather than $N_2H_5^+$ is the reactive species. For a plot of log (rate constant) as a function of log (equilibrium constant) a linear free energy relationship (LFER) with slope ~0.5 was obtained, implying that the rate-limiting step was electron transfer rather than product separation. The oxidation of N_2H_4 by $[Ru(bpy)_3]^{3+}$ has been studied, but the results are difficult in interpret because the pH was not controlled.[6] The oxidation by Fe^{III}EDTA has also been studied,[5b] but the kinetics are somewhat ambiguous because subsequent studies have shown that the complex itself undergoes a proton-dependent equilibrium under the conditions of the experiments.[7] In a recent study the oxidation by Mn^{III}(CYDTA) has been discussed in terms of an inner-sphere mechanism.[8] Other reactions of N_2H_4 have been reviewed by Stedman,[9] but none of these can reliably be assigned an outer-sphere mechanism.

One other series of oxidants that might have been expected to proceed by an outer-sphere pathway comprises the haloiridium(IV) complexes. $IrCl_6^{2-}$ is the most widely known of these, and its reaction with N_2H_4 has been investigated several times.[10-12] The reaction has been shown to form $IrCl_6^{3-}$, consistent with an outer-sphere mechanism,[10-12] and diimide (N_2H_2) has been trapped as an intermediate[11] on the way to the final products. A LFER of slope 0.45 was found for a log/log plot of the rates and equilibria of the reactions of $IrCl_6^{2-}$, $IrBr_6^{2-}$, $IrCl_5H_2O^-$, and $IrCl_4(H_2O)_2$.[11] In both of the kinetics studies,[10,11] however, it was argued that $N_2H_5^+$ was the reactive species, and in one case[10] a complex rate law was observed that required a highly unusual mechanism. Our attempts to reconcile these peculiar results with the oxidations by $Mo(CN)_8^{3-}$, $W(CN)_6^{3-}$, and $Fe(CN)_6^{3-}$ met with no success. Since both kinetics studies of the oxidation by $IrCl_6^{2-}$ were done only in highly acidic media, we have reinvestigated the reaction under a broad range of pH; the new results are somewhat contradictory to those obtained previously, but they are quite compatible with studies of the reactions with $M(CN)_x^{3-}$.

Experimental Section

Materials. $Na_2IrCl_6\cdot 6H_2O$ (Alfa) and NaCl (Baker) were used as received. $N_2H_5H_2PO_4$ (Pfaltz and Bauer) was recrystallized from hot water, and dried in a vacuum desiccator. $N_2H_4H_2SO_4$ (MCB) was recrystallized from hot water and dried in a 110 °C oven. $N_2H_4H_2SO_4$ was used in the stoichiometry studies, and $N_2H_5H_2PO_4$ was used in the kinetics experiments. $K_4Fe(CN)_6\cdot 3H_2O$ (Baker) was recrystallized as described in Perrin et al.[13] Na_2HPO_4 (Mallinckrodt) and $Na_2B_4O_7\cdot 10H_2O$ (Mallinckrodt) were recrystallized from warm water, and $NaCH_3CO_2\cdot 3H_2O$ (Mallinckrodt) was recrystallized from hot 50:50 H_2O:ethanol, as described in Perrin et al.[13] Deionized water was distilled in an all-glass Corning MP-1 still.

Solutions and Analyses. Buffer solutions were prepared by weighing the solid salts. N_2H_4 concentrations were determined by bromate titration as described in Kolthoff et al.[14] Solutions were permitted to contact only glass, platinum, and Teflon. Solutions of $IrCl_6^{2-}$ were, in addition, prepared once every 2 h to avoid complications due to hydrolysis.[15] pH of the solutions was determined with a Corning 130 pH meter at room temperature (~23 °C). Ion chromatography was performed as described by Fritz et al.[16] with a Wescan ICM

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equipped with an Eldex B-94 pump, a Pedersen MR strip chart recorder, and a 100-μL sample loop. The column was a Wescan 25-cm cation-exchange column with matching guard column. The eluant was 2×10^{-3} M HNO_3, and the flow rate was 0.73 mL/min. Peaks were detected with a Wescan 213A conductivity detector. Retention times were as follows: Na^+, 1.44 min; NH_4^+, 2.40 min; $N_2H_5^+$, 3.12 min.

Kinetics. Kinetics data were obtained with a Cary 210 UV/visible spectrophotometer and an Aminco-Morrow stopped-flow apparatus equipped with an OLIS 3820 data acquisition system as described previously.[3] The slow runs on the Cary were performed by pipetting 2.7 cm^3 of the N_2H_4/buffer solution into a 1-cm rectangular quartz cuvette, allowing the solution to come to temperature, and injecting 0.2 cm^3 of the $IrCl_6^{2-}$ solution. The rapid stopped-flow reactions were performed by mixing equal volumes of the two thermostated solutions. In all cases there was at least a 10-fold excess of N_2H_4 over $IrCl_6^{2-}$, and excellent pseudo-first-order fits were obtained. The kinetics were monitored at 487 nm, with an ionic strength of 0.20 M (NaCl) and a temperature of 25.0 °C.

In the pulse-radiolysis experiments solutions were subjected to 200-ns pulses of a 3-MeV electron beam having a Van de Graaff generator as a source. The reactions were monitored in a 1.8-cm quartz flow cell at room temperature (~22 °C) by visible absorbance measurements. Dosimetry was performed with a 1×10^{-2} M NaSCN solution that was saturated with N_2O. The absorbance at 472 nm due to $(SCN)_2^-$ ($\epsilon = 7580$ M^{-1} cm^{-1}) was taken as a measure of the yield of $OH\cdot + e^-$.[17] Solutions containing $K_4Fe(CN)_6{\cdot}3H_2O$, $N_2H_5H_2PO_4$, and Na_2HPO_4 and $HClO_4$ or NaOH were saturated with N_2O and were protected from room light; absorbance changes were monitored at 420 nm. A 400-nm UV cutoff filter (Schott GG400) was placed in the optical path before the solution to minimize photolysis.

Results

Initial studies were attempted with the hydrazinium salt of $CF_3SO_3^-$; however, the material proved to be extremely hygroscopic, and reliable results could not be obtained. Ultimately $N_2H_5H_2PO_4$ was selected because the phosphate was deemed to be unlikely to participate in radical reactions and it would also be its own buffer over a large range of pH.

Stoichiometry studies were not extensive because they have been previously performed with fairly consistent results.[11,12] However, one contradictory study reported that under the conditions of excess N_2H_4 and pH 1 the consumption ratio, $\Delta[IrCl_6^{2-}]/\Delta[N_2H_4]$, was 1 instead of 4 and that NH_4^+ was a product. We have investigated the stoichiometry at pH 3.3 and at pH 8.1 (adjusted with NaOH) with $[IrCl_6^{2-}]_0 = 1 \times 10^{-3}$ M and $[N_2H_4]_0 = 5 \times 10^{-3}$ M; ion chromatography was used to determine the yield of NH_4^+ and the consumption of $N_2H_5^+$. A solution of the above composition was prepared and allowed to react for 30 min (~10 half-lives). It was then diluted with water by a factor of 10 and injected into the chromatograph. By comparison of peak heights of the sample with those of a similar solution containing no $IrCl_6^{2-}$, a consumption ratio of 3.3 ± 0.5 was obtained; the technique appears to determine concentrations to an accuracy of ±5%, and so the specified uncertainty indicated the degree of reproducibility in the experiments. Since only a small fraction of the N_2H_4 was consumed, systematic errors could be considerably greater, but a consumption ratio of 1.0 is clearly inconsistent with our data. As shown in Figure 1 there was almost no evidence for formation of NH_4^+ in the chromatograms; in a blank experiment where NH_4Br was added to the product mixture at a concentration equal to $[IrCl_6^{2-}]_0$, a strong NH_4^+ peak was observed. It can thus be estimated that NH_4^+ was produced with a yield less than 1% of $[IrCl_6^{2-}]_0$. We also found that NH_4^+ was a contaminant in several preparations of $N_2H_5H_2PO_4$; this may account for Sengupta and Sen's qualitative detection of NH_4^+ in the product mixtures.[10] It is more difficult to account for their observed consumption ratio of 1.0, but since, as described below, their kinetics data are also inconsistent with ours, it is possible that they were observing a different reaction.

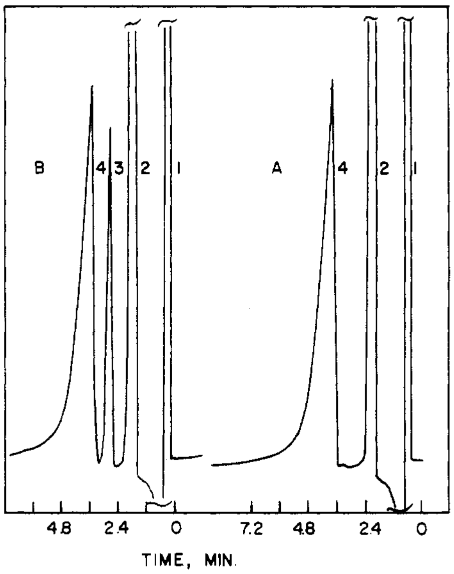

Figure 1. Ion chromatograms: (A) diluted product solution; (B) diluted product solution with 1×10^{-4} M NH_4Br added. Peak labels: (1) solvent; (2) Na^+; (3) NH_4^+; (4) $N_2H_5^+$.

Table I. Kinetics Results for the Reaction of $IrCl_6^{2-}$ with N_2H_4[a]

$[N_2H_4]_{tot}$, M	pH	k_{obsd}, s^{-1}	k_{calcd}, s^{-1}
3.83×10^{-2}	2.48	4.93×10^{-3}	2.57×10^{-3}
3.83×10^{-2}	1.99	1.78×10^{-3}	8.24×10^{-4}
3.83×10^{-2}	1.49	4.44×10^{-4}	2.64×10^{-4}
3.83×10^{-2}	1.17	1.79×10^{-4}	1.25×10^{-4}
9.68×10^{-3}	6.01[c]	1.67	2.16
9.68×10^{-3}	5.51[c]	5.53×10^{-1}	6.96×10^{-1}
9.68×10^{-3}	4.92[c]	1.45×10^{-1}	1.77×10^{-1}
9.68×10^{-3}	4.49[c]	5.94×10^{-2}	6.56×10^{-2}
9.68×10^{-3}	4.02[c]	2.21×10^{-2}	2.25×10^{-2}
9.68×10^{-3}	3.47[c]	8.67×10^{-3}	6.38×10^{-3}
9.68×10^{-3}	2.98[c]	4.17×10^{-3}	2.04×10^{-3}
1.92×10^{-3}	9.00[b]	3.40×10	3.53×10
1.92×10^{-3}	9.52[b]	3.66×10	3.75×10
1.92×10^{-3}	10.03[b]	3.79×10	3.82×10
9.67×10^{-3}	8.79	1.70×10^{2}	1.69×10^{2}
9.67×10^{-3}	8.36	1.40×10^{2}	1.39×10^{2}
9.67×10^{-3}	8.04	1.09×10^{2}	1.07×10^{2}
9.67×10^{-3}	7.52	5.36×10	5.21×10
9.67×10^{-3}	6.90	1.63×10	1.56×10
9.67×10^{-3}	6.46	6.74	6.04
7.25×10^{-3}	6.43	5.05	4.16
4.84×10^{-3}	6.38	3.32	2.53
1.45×10^{-2}	6.49	9.97	9.71
1.93×10^{-2}	6.52	1.31×10	1.36×10
2.90×10^{-2}	6.55	1.89×10	2.21×10

[a] 25.0 °C; $\mu = 0.20$ M (NaCl); $[IrCl_6^{2-}]_0 = 2 \times 10^{-4}$ M. Each value of k_{obsd} is the average of at least three runs; the precision for a given set of solutions is ±2%. [b] Borax buffer, 1×10^{-3} M. [c] Acetate buffer, 2×10^{-3} M.

Kinetics measurements were made over a broad range of pH and of N_2H_4 concentrations. Table I presents these results in terms of the total (titratable) hydrazine concentration $[N_2H_4]_{tot}$, the measured pH, and the pseudo-first-order rate constant, k_{obsd}. A series of measurements at pH ~6.5 demonstrates a good first-order dependence on $[N_2H_4]_{tot}$. The pH dependence is more complex; at high pH there is no dependence, but at lower pH the reaction is inhibited. This is illustrated in Figure 2 as a plot of log $(k_{obsd}/[N_2H_4]_{tot})$ vs. pH,

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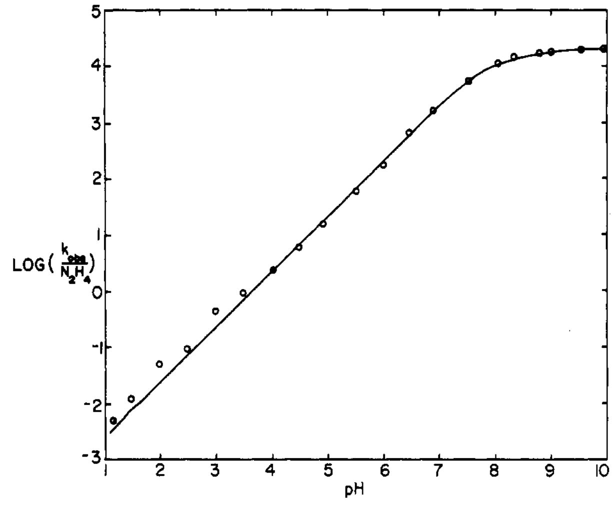

Figure 2. pH dependence of the kinetics of oxidation of N_2H_4 by $IrCl_6^{2-}$: log $[k_{obsd}/[N_2H_4]_{tot}]$ vs. pH (25.0 °C; $\mu = 0.20$ M (NaCl); $[IrCl_6^{2-}]_0 = 2 \times 10^{-4}$ M; $[N_2H_4]_{tot} = 1.9 \times 10^{-3}$ to 3.8×10^{-2} M). The solid curve is the computer fit.

where the slope shifts from 1 to 0 near pH 8.

These observations suggest the rate law (1). A nonlinear least-squares fit of eq 1 to the data yields $k' = (2.01 \pm 0.03)$

$$k_{obsd} = \frac{k'[N_2H_4]_{tot}}{1 + [H^+]/K''} \qquad (1)$$

$\times 10^4$ M^{-1} s^{-1} and $K'' = (1.10 \pm 0.03) \times 10^{-8}$ M under the approximation that $[H^+] = 10^{-pH}$. Table I includes values of k_{calcd} from this fit; the deviations between k_{obsd} and k_{calcd} are quite acceptable above pH 4. Below pH 4 k_{calcd} is consistently less than k_{obsd}, sometimes by as much as a factor of 2. This may be due to a specific medium effect as the buffer is changed, or it may be due to other effects as described below.

These results differ from those previously obtained.[10,11] Both prior studies were carried out at high ionic strengths (1–2 M) and at high acidities (pH 2–pH 0). One asserts[11] (although no data are presented) that the reaction is first order in $[N_2H_4]_{tot}$, while the other[10] shows saturation kinetics at high $[N_2H_4]_{tot}$ (although the ionic strength appears not to have been controlled). The data of the two studies are in rough agreement in that a plot of $1/k_{obsd}$ vs. $[H^+]$ is linear with a positive intercept (although the values of the intercepts are not in agreement); limiting rates are achieved at about pH 2, but inhibition occurs at higher acidities. These observations are in contrast with our Figure 2. Furthermore, specific values of $k_{obsd}/[N_2H_4]_{tot}$ at pH 1 are greater than ours by factors of 10–20.[11] The instability of $IrCl_6^{2-}$ in alkaline media cannot be the source of the disagreement, because the decomposition is roughly first order in $[OH^-]$, and even at pH 13 the half-life (~5 min) is much greater than that found at pH 10 for the oxidation of hydrazine.

We are at a loss to explain the discrepancies, but in view of the peculiar mechanisms that the previous studies have invoked to explain their results and the simplicity of our results and mechanism (see below), we suggest that the prior studies in acid media may be in error. Residual effects of these complications may be the reason for the discrepancy shown in Figure 2 at pH <4. However, the emphasis of this paper is on the limiting behavior in alkaline media.

Pulse radiolysis studies were undertaken to determine the rate constant for the reaction of $N_2H_4^+$ with $Fe(CN)_6^{4-}$. A solution was prepared with $[Fe(CN)_6^{4-}] = 1 \times 10^{-3}$ M, $[N_2H_4]_{tot} = 1 \times 10^{-2}$ M, and $[Na_2HPO_4] = 1 \times 10^{-2}$ M, and it was adjusted to pH 5; it was then saturated with N_2O to convert e^- to OH·. The solution was irradiated with 1 dose equiv to an initial yield of OH· + e^- of 6.8×10^{-6} M. A prompt rise in absorbance was observed during the first 2 μs, and over the subsequent 180 μs no further changes were observed. Since $\epsilon_{420} = 1.0 \times 10^3$ M^{-1} cm^{-1} for $Fe(CN)_6^{3-}$ while for $Fe(CN)_6^{4-}$ ϵ_{420} is effectively 0,[18] the prompt absorbance rise implies a prompt yield of $Fe(CN)_6^{3-}$ of 47% of the initial yield of e^- + OH·. A comparable theoretical yield of 54% may be calculated on the assumption that the prompt reaction is due to the competition of $Fe(CN)_6^{4-}$ and $N_2H_5^+$ for OH·. This calculation uses rate constants of 1.2×10^{10} M^{-1} s^{-1} for the reaction of $Fe(CN)_6^{4-}$ with OH·[18] and 1.0×10^9 M^{-1} s^{-1} for the reaction of $N_2H_5^+$ with OH·.[19] Since half of the primary radicals were consumed by $Fe(CN)_6^{4-}$, the yield of $N_2H_4^+$ was 3.4×10^{-6} M. The recombination rate constant of $N_2H_4^+$ at this pH is 6.0×10^8 M^{-1} s^{-1} (=2 k),[18] and so the intrinsic half-life was 490 μs. The failure to observe a slow process on this time scale, yielding $Fe(CN)_6^{3-}$, thus sets for the process

$$Fe(CN)_6^{4-} + N_2H_4^+ \rightarrow Fe(CN)_6^{3-} + N_2H_4 \qquad (2)$$

an upper limit of $\sim 3 \times 10^6$ M^{-1} s^{-1}.

Similar results were obtained at pH 8; the prompt yield of $Fe(CN)_6^{3-}$ was only 14%, as expected, since at this pH the hydrazine is 50% deprotonated,[20] and the rate of reaction of N_2H_4 with OH· is 1.4×10^{10} M^{-1} s^{-1},[18] i.e., a factor of 14 faster than that of $N_2H_5^+$. Again, no direct reaction of $N_2H_4^+$ (or N_2H_3) with $Fe(CN)_6^{4-}$ was detected.

Discussion

Prior studies[10-12] have provided convincing evidence that the stoichiometry of the reaction is

$$4IrCl_6^{2-} + N_2H_4 \rightarrow 4IrCl_6^{3-} + N_2 + 4H^+ \qquad (3)$$

when $IrCl_6^{2-}$ is present in large excess. Sengupta and Sen[10] reported that the stoichiometry is

$$IrCl_6^{2-} + N_2H_5^+ \rightarrow IrCl_6^{3-} + {}^1/_2N_2 + NH_4^+ + H^+ \qquad (4)$$

in 0.1 M acid when N_2H_4 is in excess, but we have found that at pH 3.3 with excess N_2H_4 eq 3 is correct. The reaction throughout the remainder of this paper is discussed in terms of eq 3. A simple mechanism is as follows:

$$N_2H_5^+ \rightleftarrows N_2H_4 + H^+ \quad K_a \qquad (5)$$

$$IrCl_6^{2-} + N_2H_4 \rightarrow N_2H_4^+ + IrCl_6^{3-} \quad k_1 \qquad (6)$$

$$3IrCl_6^{2-} + N_2H_4^+ \xrightarrow{\text{fast}} 3IrCl_6^{3-} + N_2 + 4H^+ \qquad (7)$$

If it is assumed that the fast steps following k_1 proceed by three subsequent one-electron oxidations, then rate law (8) can be derived.

$$\frac{-d[IrCl_6^{2-}]}{dt} = \frac{4k_1[IrCl_6^{2-}][N_2H_4]_{tot}}{1 + [H^+]/K_a} \qquad (8)$$

derived. Thus, k' is identified as $4k_1$, and K'' is K_a. Our measured value of K_a (1.1×10^{-8} M) is in reasonable agreement with a literature value (8.7×10^{-9} M at $\mu = 0.5$ M).[20] The hydrazinium radical cation, $N_2H_4^+$, has been identified and characterized in aqueous solution by the technique of pulse radiolysis.[19] Certain aspects of this work have been subject to revision, i.e., the pK_a of the intermediate, $N_3H_4^+$,[21] and the recombination reactions.[22] However, the measurement of the acidity of $N_2H_4^+$ (pK_a = 7.1) remains reliable. Since dimerization of N_2H_3 leads to formation of NH_3,[21] which is not formed in the oxidation by $IrCl_6^{2-}$, and since N_2H_2 was detected as an intermediate,[11] it is fairly certain that the fate of $N_2H_4^+$ is some combination of pH-dependent deprotonation and oxidation by $IrCl_6^{2-}$ to form N_2H_2. There is scant in-

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formation on the behavior of N_2H_2 in aqueous solution,[9] and its path to N_2 may only be guessed. The factor of 4 in eq 8 is therefore uncertain; another possibility would be 2 if, for example, N_2H_2 were to disproportionate to N_2 and N_2H_4. Perhaps the fate of N_2H_2 differs in acidic and alkaline media, resulting in a shift of this factor; this could explain the discrepancy in the fit in Figure 2.

If it is assumed that 4 is the correct factor in eq 8, then k_1 is 5.03×10^3 M^{-1} s^{-1}. A similar treatment of the data of Leipoldt et al.[4] gives for the oxidation of N_2H_4 by $Mo(CN)_8^{3-}$ a k_1 value of 2.14×10^3 M^{-1} s^{-1}. $IrCl_6^{2-}$ is a stronger oxidant ($E° = 0.892$ V[23]) than $Mo(CN)_8^{3-}$ ($E° = 0.75$ V[24]) and so the greater rate is as expected. The rate constant ratio for the oxidations of N_2H_4 by $IrCl_6^{2-}$ and $Mo(CN)_8^{3-}$ of 2.4 may be compared with ratios spanning 3.3–8.5 for oxidations of the similarly charged substituted benzenediols.[25] (The ratio for the parent benzene-1,2-diol of 28.4 appears to be anomalous.) A careful comparison in terms of Marcus–Hush theory would entail a correction for the differing charge types and the free energy changes. Unfortunately, the reduction potential for $N_2H_4^+$ is unknown.

Estimates of the reduction potential for $N_2H_4^+$ from gas-phase data are unreliable because the photoelectron spectrum of N_2H_4 yields only a vertical ionization energy[26] and the heat of formation of N_2H_3 is highly uncertain.[27] A good upper limit for $E°$ can be obtained by considering the reaction of $Fe(CN)_6^{3-}$ with N_2H_4. This reaction presumably has a rate-limiting step (k_1) as described in eq 9. The forward rate

$$N_2H_4 + Fe(CN)_6^{3-} \rightleftarrows N_2H_4^+ + Fe(CN)_6^{4-} \quad k_1, k_{-1} \qquad (9)$$

constant, k_1, has been measured,[4] and the reverse rate constant, k_{-1}, may be assigned a diffusion-controlled upper limit of 1×10^{10} M^{-1} s^{-1}. The ratio, k_1/k_{-1}, is the equilibrium constant for this step; by using the known reduction potential for $Fe(CN)_6^{3-}$, $E° \leq 0.94$ V for the $N_2H_4^+/N_2H_4$ couple can be calculated. When this $E°$ is combined in a similar manner with $E°$ for the $IrCl_6^{2-}/IrCl_6^{3-}$ couple and our measured rate of oxidation of N_2H_4 by $IrCl_6^{2-}$, it is found that the reduction of $N_2H_4^+$ to N_2H_4 by $IrCl_6^{3-}$ has a rate constant less than 3.3×10^4 M^{-1} s^{-1}. This is substantially less than diffusion controlled, and so the oxidation of N_2H_4 by $IrCl_6^{2-}$ must have a kinetic barrier that is significantly greater than that imposed by the energetics of the intermediates.

A tighter constraint on $E°$ for $N_2H_4^+$ may be obtained from the pulse-radiolytic observation that, for reduction of $N_2H_4^+$ by $Fe(CN)_6^{4-}$, $k \leq 3 \times 10^6$ M^{-1} s^{-1}. Combining this upper limit with the measured rate constant for reaction of N_2H_4 with $Fe(CN)_6^{3-}$ as described above gives $E° \leq 0.73$ V for $N_2H_4^+$. Therefore, the reaction of $IrCl_6^{2-}$ with N_2H_4 is actually thermodynamically favorable in the first step. A crude calculation of the effective self-exchange rate constant for the $N_2H_4/N_2H_4^+$ couple by using the equation $k_{11} = k_1^2/(K_{eq}k_{22})$ gives $k_{11} < 3 \times 10^{-1}$ M^{-1} s^{-1}.[28] In this context the self-exchange rate constant of 9×10^{-6} M^{-1} s^{-1} for the $ON(SO_3)_2^{2-}/ON(SO_3)_2^{3-}$ couple, obtained by Balasubramanian and Gould, is noteworthy.[29]

Hydrazine has a gauche geometry, but ESR studies are consistent with a planar hydrazinium radical.[30] On the basis of INDO calculations the N–N bond length of N_2H_4 has been reported to shorten by 18 pm on oxidation.[31] These large changes in geometry should be responsible for a major portion of the kinetic barrier; similar arguments have been advanced by Nelsen for oxidations of a variety of sterically unconstrained alkylhydrazines.[32]

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Registry No. N_2H_4, 302-01-2; $IrCl_6^{2-}$, 16918-91-5; $Fe(CN)_6^{4-}$, 13408-63-4; $N_2H_4^+$, 20771-51-1.

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