Large Reorganization Energies in Electron Transfer: Oxidation of Hydroxylamine by Hexachloroiridate(IV)

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Oxidation of NH_2OH (designated N(−1)) by $[IrCl_6]^{2-}$ in aqueous solution is catalyzed by Cu^{2+} and Fe^{2+}, but the effects of these ions can be thoroughly inhibited by $C_2O_4^{2-}$. In the presence of this inhibitor and with excess N(−1), the rate law is $-d[IrCl_6^{2-}]/dt = k_1K_a[IrCl_6^{2-}][N(-1)]/([H^+] + K_a)$ with $k_1 = 24 \pm 5$ M^{-1} s^{-1} and $K_a = (6.7 \pm 1.7) \times 10^{-7}$ M at $\mu = 0.1$ M, 25 °C, and pH (4.23−6.78). The K_a value refers to the deprotonation of NH_3OH^+, while k_1 is inferred to be the rate constant of electron transfer from NH_2OH to $[IrCl_6]^{2-}$. An analysis of k_1 in terms of the cross relationship of Marcus theory leads to an estimated self-exchange rate constant of 5×10^{-13} M^{-1} s^{-1} ($\lambda = 530$ kJ mol^{-1}) for the NH_2OH^+/NH_2OH redox couple, which is in agreement with the predictions of ab initio calculations.

Introduction

Hydroxylamine (NH_2OH) is a major item of commerce. Its principal use is in the synthesis of caprolactam, but it has many other applications as well.[1] It also appears as an intermediate in the oxidation of ammonia by nitrifying bacteria, and its oxidation to nitrite is catalyzed by the heme-containing enzyme hydroxylamine oxidoreductase.[2] Oxidation of NH_2OH in simple inorganic systems has been studied extensively.[3] Free radicals derived from its oxidation by Ce(IV) and $[Fe(CN)_6]^{3-}$ have been detected by ESR,[4,5] and they have been proposed as intermediates in other oxidations, such as by $[W(CN)_8]^{3-}$ and $[IrCl_6]^{2-}$.[6-8] An intriguing question suggested by the above is whether hydroxylamine can undergo oxidation by simple electron transfer and, if so, whether the rates can be understood in terms of an outer-sphere mechanism and correlated with Marcus theory.

A search of the literature for reactions of this type reveals a very limited set of candidates. The oxidation by ferricyanide was originally reported to be first order with respect to both NH_2OH and $[Fe(CN)_6]^{3-}$,[9] but subsequently it was discovered to be so sensitive to catalysis by trace levels of Cu^{2+} that no information could be derived regarding the uncatalyzed process.[10] In the presence of EDTA, catalysis was still a problem because of the activity of Fe^{III}(EDTA) (formed from trace contamination by Fe ions). The oxidation by $[IrCl_6]^{2-}$ in acidic media was found to be first order with respect to $[IrCl_6^{2-}]$ and $[NH_3OH^+]$, and inverse order with respect to $[H^+]$;[7] a very recent report on the same reaction but at somewhat higher pH showed a more complex rate law, with inhibition by Cl^-.[8] Neither of these studies reported experiments to test for metal ion catalysis, although it has been claimed elsewhere that this reaction is extremely sensitive to trace Cu^{2+} catalysis.[11] Another pertinent reaction is the oxidation by $[W(CN)_8]^{3-}$, which was reported to have three paths, corresponding to oxidation of NH_3OH^+, NH_2OH, and NH_2O^-; the possibility of copper catalysis was not mentioned nor were precautions taken to prevent it.[6]

We recently reported a series of oxidations of $S_2O_3^{2-}$, which were strongly catalyzed by trace metal ions. This catalysis was successfully inhibited by the addition of phenanthroline or oxalate, thus allowing the direct electron-transfer rate constants to be measured.[12,13] With this experience in hand, we decided to return to the question of electron-transfer oxidation of NH_2OH. $[IrCl_6]^{2-}$ was selected as the oxidant because it is convenient to use, reacts with NH_2OH at acceptable rates, and is relatively free of complications arising from ligand substitution processes. Although use of this oxidant does not ensure an outer-sphere mechanism, it can provide a useful benchmark of reactivity, and in the present case it appears to approach the outer-sphere limit rather closely.

Experimental Section

All chemicals, methods, and laboratory instruments for this study were the same as described previously, except as specified below.[14] Chemicals which were of reagent or analytical grade were stored in the dark or under subdued lighting conditions. $Na_2IrCl_6{\cdot}6H_2O$ (Alfa), N_2O (Matheson), K_2IrCl_6 (Aldrich), and $(NH_2OH)_2{\cdot}H_2SO_4$ (Aldrich) were used as purchased. $NH_2OH{\cdot}HCl$ (Baker) was recrystallized from MeOH; it was established to have an excellent level of purity by IR and ^1H NMR spectroscopies and was used in all experiments except as indicated. Initial concentrations of all compounds in solution were established by weight.

Buffer solutions for all reactions were maintained by $NH_2OH{\cdot}HCl$, NaOH, and $Na_2C_2O_4$. $Na_2C_2O_4$ also fills the role of chelating agent. $IrCl_6^{2-}$ is unstable in alkaline solution;[15] likewise, hydroxylamine

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solutions decompose in anaerobic alkaline media, but the effect is significant only when the hydroxide concentration exceeds 1 M.[16] Hydroxylamine solutions also undergo alkaline autoxidation, but this is catalyzed by metal ions and inhibited by chelates.[17-19] Hence, chemicals used to adjust the buffer were added to the hydroxylamine solution. For reactions to be conducted anaerobically, solutions were prepared with water sparged with Ar and then sparged with Ar for a further 10−15 min prior to initiation of the reaction. Solutions for other reactions were prepared freshly. All reactions were conducted under diminished lighting conditions.

Ion chromatographic techniques were employed in the analysis of ions produced in this reaction as described previously.[14] Cation analyses were performed with a 25 cm resin-based Wescan cation exchange column, conductivity detection, and 1.98 mM HNO_3 flowing at 2.0 mL min^{-1} as the eluent. Under these conditions, the peaks due to Na^+ and NH_3OH^+ overlapped, and hence K_2IrCl_6 and $Li_2C_2O_4$ were used instead of sodium salts. NH_3OH^+ was detected with a retention time of 1.8 min. Anion analyses used a 10 cm Wescan silica-based anion exchange column, with 5.0 mM phthalic acid flowing at 2.0 mL min^{-1} as the eluent. Chloride was detected with amperometric detection at a Ag working electrode at 200 mV vs Ag/AgCl, while conductivity was used to detect NO_2^-, NO_3^-, and SO_4^{2-}. For the anion analysis, $(NH_2OH)_2{\cdot}H_2SO_4$ was used instead of $NH_2OH{\cdot}HCl$ so as to permit detection of Cl^- as a potential product. This species had a retention time of 4.2 min.

N_2O was analyzed by use of an IBM FTIR with a 10 cm gas phase IR cell as described previously.[20] For each run, the cell was evacuated to at least 10^{-4} Torr and a blank spectrum was recorded. A 50 mL round-bottom flask containing 10 mL of solution was then connected to the cell; the head space gas was admitted to the cell and allowed 10 min to equilibrate. The absorbance due to N_2O at 2236 cm^{-1} was measured. The yield of N_2O was then determined by use of a calibration curve that was obtained from samples of a serially diluted stock solution of H_2O saturated with N_2O ($[N_2O]_{satd} = 2.4 \times 10^{-2}$ M/atm).[21]

For kinetics studies, the reactions were thermostated at 25 °C and monitored at 488 nm by a Hewlett-Packard 8452A spectrophotometer and a Hi-Tech SF-51 stopped-flow. Pseudo-first-order rate constants were evaluated by use of the OLIS 4300S data acquisition and analysis system; the Kaleidagraph data analysis/graphics application was used to analyze the values of k_{obs}.

The entropy of NH_2O was calculated with the AM1 method by use of MOPAC 6.0 running on a Macintosh IIci computer.[22] Ab initio calculations were performed with the Gaussian 92 package.[23] The transition-state geometry for the self-exchange reaction between NH_2OH and NH_2OH^+ was located by optimizing the geometry of a supermolecule containing both species separated by 100 Å under the constraint that they both have the same geometries; this optimization was performed at the UMP2 level with the NOSYMM option so as to permit charge localization on one of the molecules.

Results

Stoichiometry. Ion chromatography was used to determine the production of anions and the consumption of hydroxylamine in its reaction with $[IrCl_6]^{2-}$. SO_4^{2-} (from the $(NH_2OH)_2{\cdot}H_2SO_4$ reactant) and Cl^- were observed in the product solution. Neither NO_2^- nor NO_3^- was observed in an experiment with 13 mM N(−1) and 0.64 mM $[IrCl_6]^{2-}$, our detection limit for both species being about 20 μM. Studies on the yield of Cl^- were performed on the products from a mixture of 2.3 mM N(−1) (total hydroxylamine) and 0.30 mM $[IrCl_6]^{2-}$ at pH 6.4. A chloride concentration of 28 μM was observed immediately after the reaction, and it rose to 91 μM after 1 h. Thus, less than 10% of the $[IrCl_6]^{n-}$ releases Cl^- during reaction, and therefore over 90% of $[IrCl_6]^{2-}$ reacts directly with hydroxylamine to form $[IrCl_6]^{3-}$. Note that this is a much more sensitive test for aquation than the conventional method of UV−vis analysis of a chlorinated solution of the products.

The consumption of hydroxylamine was determined as follows. A reaction mixture of 0.10 mM K_2IrCl_6 with 0.406 mM N(−1) and 1.0 mM $Li_2C_2O_4$ at ca. 23 °C and pH 5.2 was prepared by using deionized water purged with Ar. After the $[IrCl_6]^{2-}$ was consumed, the solution was analyzed by ion chromatography and compared with a calibration curve for $[NH_3OH^+]$. This experiment led to a consumption ratio, $\Delta[NH_3OH^+]/\Delta[IrCl_6^{2-}]$, of 0.98.

As determined by FTIR head space analysis, the reaction of 2.05 mM $[IrCl_6]^{2-}$ with 30.0 mM N(−1) in 1.0 mM oxalate (pH 6.0, ~23 °C) generated 0.205 mM N_2O. Although this is a relatively small yield of N_2O, it would require a value for $\Delta[NH_3OH^+]/\Delta[IrCl_6^{2-}]$ significantly less than reported above. Presumably, our observed yield of N_2O is a consequence of the high initial concentration of $[IrCl_6]^{2-}$. With low initial concentrations of $[IrCl_6]^{2-}$, as in the kinetics studies, to a good approximation the reaction is given by

$$[IrCl_6]^{2-} + NH_3OH^+ \rightarrow [IrCl_6]^{3-} + {}^1\!/_2N_2 + 2H^+ + H_2O \quad (1)$$

which is in agreement with the stoichiometry reported by Sen et al.[7] Our observation of partial conversion to N_2O at high ratios of $[Ir(IV)]_0/[N(-1)]$ is in agreement with the observations of Rekha et al.;[8] these workers also obtained a high yield of $[IrCl_5(H_2O)]^{2-}$, but their experments were conducted under conditions where the reaction was very slow so that the $[IrCl_6]^{3-}$ product had sufficient time to aquate.[8]

Kinetics. Reactions were studied with a large excess of hydroxylamine and were conducted at 0.1 M ionic strength (maintained with $NaClO_4$) and 25 °C. Under these conditions the reactions obeyed pseudo-first-order kinetics with residuals always less than 2%. Preliminary studies revealed two catalytic effects that, if not properly controlled, could lead to misleading or irreproducible behavior, as described below. Neither of these effects was described in the prior reports on this reaction.[7,8]

Effects of Transition Metal Ions and a Chelate. Tests for the effects of divalent metal ions as potential impurities were performed by adding 0.1 mM Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} to a 0.04 M N(−1) solution. The solution of NH_2OH with Cu^{2+} was pale yellow-green, and with Fe^{2+} it was light yellow with slight turbidity. The other solutions were clear and colorless. These solutions were then mixed in a stopped-flow instrument with an equal volume of 0.2 mM $[IrCl_6]^{2-}$ solution at pH ca. 5.9 (buffer adjusted with NaOH). After mixing, the absorbance due to $[IrCl_6]^{2-}$ in the reaction containing Fe^{2+} dropped to zero in about 2 ms (only half of the consumption being attributable to the direct reaction of $[IrCl_6]^{2-}$ with Fe^{2+}),[24] and with Cu^{2+} the reaction was complete within the dead time of the instrument (<2 ms). However, when the additives were Mn^{2+}, Ni^{2+}, and

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Co^{2+}, the reaction had a half-life of a few seconds, the same as if no metal ions were added. Apparently, Fe^{2+} and Cu^{2+} are very effective catalysts.

Tests of the effectiveness of oxalate as an inhibitor were performed with $[IrCl_6^{2-}]_0 = 0.1$ mM, $[N(-1)] = 20$ mM, and pH ~5.9. Under these conditions 1 mM oxalate completely inhibited the catalytic effect of 0.05 mM Fe^{2+}. However, 2 mM oxalate was required to inhibit catalysis by 0.05 mM Cu^{2+}. In another series of experiments conducted under the above conditions (except with 30 mM N(−1)), it was found that 1 mM oxalate was sufficient to inhibit catalysis by adventitious metal ions and that higher concentrations of oxalate had no further effect. Without oxalate, the rate constants were about 7 times greater due to the effect of impurity ions. Previous reports indicate that the direct reaction of $IrCl_6^{2-}$ with oxalate is quite slow,[25,26] and hence it is not significant in our stopped-flow experiments. All further experiments were conducted with 1 mM oxalate in the reaction mixtures.

Degradation Effects. In further preliminary experiments, it was found that the rates were mildly sensitive to the batch of $[IrCl_6]^{2-}$ used. Thus, when a sample of commercial K_2IrCl_6 was used, the rates were about twice as fast as when a highly crystalline sample of commercial $Na_2IrCl_6 \cdot 6H_2O$ was used. More rapid rates were also obtained when a locally-prepared sample of $Na_2IrCl_6 \cdot 6H_2O$ was used. UV−vis spectral analysis did not reveal a significant difference between the three samples. These results were taken to suggest that small amounts of aquoiridium impurities could be catalysts, since their spectra do not differ drastically from that of pure $[IrCl_6]^{2-}$.[27]

An experiment to test whether such aquo complexes could be catalytic was performed under the conditions of 0.1 mM $[IrCl_6^{2-}]_0$, 1 mM $C_2O_4^{2-}$, and pH ~6. One reactant solution contained 10 mM [N(−1)] to which had been added 0.125 mM $[IrCl_6]^{2-}$. This addition generated a reactant solution containing $[IrCl_6]^{3-}$, which undergoes slow aquation.[28,29] The pseudo-first-order rate constants obtained with this solution systematically increased with age, being, for example, 50% greater after 8 min. A similar aging experiment performed with a N(−1) solution to which $[IrCl_6]^{2-}$ had not been added showed no such acceleration.

An explanation of the above observations is that although $[IrCl_6]^{2-}$ is relatively substitution inert, $[IrCl_6]^{3-}$ is not as robust and aquates to form mono-, di-, and triaquo complexes.[28,29] Electron transfer will occur between these species and $[IrCl_6]^{2-}$, and subsequent oligomerization in both oxidation states[30] causes the formation of a variety of aqua−halo Ir(IV) complexes, some of which could be more reactive than $[IrCl_6]^{2-}$ and would thus act as catalysts. Such species could also be present in impure samples of $[IrCl_6]^{2-}$. While the effect can be significant, it is not overwhelming, and we believe that the data obtained from our best sample of $Na_2IrCl_6 \cdot 6H_2O$ are trustworthy.

Table 1. Kinetic Dependence on [N(−1)] and pH[a]

[N(−1)], mM	pH	k_{obs}, s^{-1}	[N(−1)], mM	pH	k_{obs}, s^{-1}
1.00	5.81	1.09×10^{-2}	20.8	4.23	6.22×10^{-3}
3.01	5.88	2.51×10^{-2}	15.2	4.42	7.05×10^{-3}
5.01	5.91	3.74×10^{-2}	15.0	4.52	8.56×10^{-3}
8.02	5.87	5.57×10^{-2}	20.0	4.92	2.75×10^{-2}
10.0	5.90	7.23×10^{-2}	20.1	5.41	6.54×10^{-2}
15.0	5.88	1.08×10^{-1}	20.3	5.86	1.66×10^{-1}
30.1	5.90	2.35×10^{-1}	20.0	6.78	5.48×10^{-1}

[a] Conditions: $[IrCl_6^{2-}]_0 = 0.10$ mM, $[C_2O_4^{2-}] = 1.0$ mM, $\mu = 0.1$ M ($NaClO_4$), and 25 °C.

Rate Law. The values of k_{obs} were sensitive to the concentrations of both N(−1) and H^+. The data in Table 1 show an essentially first-order dependence of k_{obs} on [N(−1)] at approximately constant pH. At hydroxylamine concentrations higher than those shown in Table 1 the rates accelerated markedly, apparently due to a higher-order term in the rate law. The rates were unaffected by sparging of the reactants with Ar. The pH-dependent data in Table 1 show a roughly inverse dependence of k_{obs} on $[H^+]$ over the range pH 4.2−6.8. Unfortunately, it was not possible to conduct experiments at pH values significantly greater than the pK_a of NH_3OH^+ (pK_a ~ 6) because of the instability of $[IrCl_6]^{2-}$ under such conditions.[15] Nevertheless, a plot of $\log(k_{obs}/[N(-1)])$ vs pH shows some curvature at high pH, which suggests that the reactive form of N(−1) is NH_2OH. A more exact treatment of these results is obtained by fitting the data with eq 2. This fit leads

$$k_{obs} = \frac{k_1 K_a [N(-1)]}{[H^+] + K_a} \tag{2}$$

to values of 24 ± 5 $M^{-1}\,s^{-1}$ for k_1 and $(6.7 \pm 1.7) \times 10^{-7}$ M for K_a ($pK_a = 6.17$). The relatively large uncertainties in these parameters arise because the experiments did not extend to sufficiently high pH to define K_a precisely. Nevertheless, the good agreement between our value of pK_a and those of other reports ($pK_a = 5.98$ at $\mu = 0.245$ M)[31] supports our assertion that NH_2OH is the reactive state of protonation. The overall rate law is

$$-\frac{d[IrCl_6^{2-}]}{dt} = \frac{k_1 K_a [IrCl_6^{2-}][N(-1)]}{[H^+] + K_a} \tag{3}$$

The first prior study[7] of this reaction was conducted at 30 °C over the range pH 1−2 and hence is not strictly comparable with ours. However, the reported rate law has the form

$$-\frac{d[IrCl_6^{2-}]}{dt} = \frac{k_{sp}[IrCl_6^{2-}][NH_3OH^+]}{[H^+]} \tag{4}$$

with $k_{sp} = 8 \times 10^{-3}\ s^{-1}$. Our rate law assumes the same form at low pH, but our equivalent rate constant, k_1K_a, has value of $1.6 \times 10^{-5}\ s^{-1}$, i.e., less by a factor of about 500.

The second prior study included data at 25 °C from pH 3.4 to 5.2 and hence is more directly comparable with our work.[8] These workers reported that the reaction was inhibited by Cl^- and that in the absence of Cl^- the rate law was

$$k_{obs} = \frac{k_{1,R} k_{et} K_{os} [N(-1)]}{k_{1,R}[H^+] + k_{et} K_{os}} \tag{5}$$

with $k_{1,R} = 147\ M^{-1}\,s^{-1}$ and $k_{et}K_{os} = 2.8 \times 10^{-2}\ s^{-1}$ at 25 °C. This rate law is equivalent to ours if $k_{et}K_{os}/k_{1,R} = K_a$ and if $k_{1,R} = k_1$. Numerically, however, the results are not equivalent, with our value of K_a being a factor of 284 lower than their value of $k_{et}K_{os}/k_{1,R}$ and our value of k_1 being a factor of 6.1 lower than

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their value of $k_{1,R}$. The general result is that, for a given set of conditions, our pseudo-first-order rate constants are always much lower than theirs. The much greater rates reported in both prior studies must have been due to unrecognized catalysis by Fe^{2+}, Cu^{2+}, or aquoiridium impurities. It is possible that the chloride inhibition described in the second report is due to chloride binding to the catalytic aquoiridium species.

Discussion

A mechanism that is consistent with the stoichiometric and kinetic data is as follows:

$$NH_3OH^+ \rightleftarrows NH_2OH + H^+ \qquad K_a \qquad (6)$$

$$[IrCl_6]^{2-} + NH_2OH \rightleftarrows [IrCl_6]^{3-} + NH_2OH^+ \qquad k_1, k_{-1}, K_1 \qquad (7)$$

$$NH_2OH^+ \rightleftarrows NH_2O + H^+ \qquad K_{a,rad} \qquad (8)$$

$$NH_2O \rightleftarrows NHOH \qquad K_{iso} \qquad (9)$$

$$2NHOH \rightarrow N_2 + 2H_2O \qquad (fast) \qquad (10)$$

Under conditions where reaction 7 is irreversible, this mechanism leads to the observed rate law, with the rate-limiting step being electron transfer from NH_2OH to $[IrCl_6]^{2-}$.

The nature of the intermediate free radicals requires some comment. From ESR studies it is clear that a radical can be generated by oxidation of NH_2OH, and the hyperfine splittings unambiguously identify this species as NH_2O in nonacidic media.[4,5,32-34] The formation of NH_2OH^+ in acidic media is also well established, and UV spectra imply that it has a $pK_{a,rad}$ of 4.2 .[35,36] However, Simic and Hayon asserted that this $pK_{a,rad}$ referred to formation of NHOH rather than NH_2O; this assignment was based on the similarity between the strong absorption at 217 nm displayed by both "NHOH" and $NHOCH_3$. Apparently these authors overlooked the fact that nitroxide radicals (NR_2O) also absorb strongly in this region of the UV.[37] Further support for the neutral radical being NH_2O comes from ab initio calculations on these species in the gas phase, which indicate NH_2O to be more stable by 24 kJ mol^{-1}.[38] Thus, we believe that the measured $pK_{a,rad}$ refers to formation of NH_2O, as indicated in reaction 8. Rapid isomerization to the NHOH form as in reaction 9 is modestly endothermic, but it leads to a form that can easily react to give N_2 as in reaction 10.

An important assumption of the above mechanism is that the electron transfer step, k_1, is irreversible. An estimate of the equilibrium constant, K_1, is helpful here, but it depends on knowledge of $E°$ for the NH_2OH^+/NH_2OH redox couple. Unfortunately, the only reported estimate of this $E°$ value ($E° < 1.26$ V)[11] was based on the erroneous prior report on the kinetics of this reaction.[7] Our new estimate is based on an ab initio calculation on NH_2O, in which $\Delta_f H°$ for this species was evaluated as 16.2 kcal/mol at 298 K.[38] A value for $S°$ of 227 J K^{-1} mol^{-1} was obtained with an AM1 calculation, which leads to $\Delta_f G° = 98$ kJ mol^{-1} for NH_2O in the gas phase. As a rough estimate, the free energy of hydration may be taken as -10 kJ mol^{-1} by analogy with NH_3, which leads to a value of 88 kJ mol^{-1} for $\Delta_f G°$ for aqueous NH_2O. Combining this with the $pK_{a,rad}$ of NH_2OH^+ mentioned above leads to a value of 64 kJ mol^{-1} for $\Delta_f G°$ for aqueous NH_2OH^+. Finally, use of the value[39] of $\Delta_f G° = 23.4$ kJ mol^{-1} for aqueous NH_2OH leads to a value of 0.42 V for $E°$ for the NH_2OH^+/NH_2OH redox couple. By use of $E_f = 0.892$ V for the $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ redox couple,[40] a value of 9×10^7 can be calculated for K_1. Given the various estimates involved in deriving this result, it cannot be very accurate, but it is sufficient to demonstrate that the back electron transfer process in reaction 7 can be neglected.

It is of interest to examine the electron transfer step in terms of an outer-sphere mechanism. Accordingly, a calculation was performed by use of the Marcus cross relation that included work terms and the effects of the f term,[41] and it was found that a self-exchange rate constant of 5×10^{-13} M^{-1} s^{-1} for the NH_2OH^+/NH_2OH redox couple would reproduce the observed value for k_1. This is an extraordinarily low self-exchange rate constant, being to our knowledge the lowest ever reported by several orders of magnitude. It corresponds to a λ_{11} value ($= 4\Delta G^{\ddagger}$) of 530 kJ mol^{-1}. The only comparable main-group self-exchange rate constant is 9×10^{-6} M^{-1} s^{-1}, reported for the $ON(SO_3)_2{}^{2-}/ON(SO_3)_2{}^{3-}$ redox couple.[42] Eberson et al. have estimated a theoretical internal reorganizational energy (λ_i) of 446 kJ mol^{-1} for the $NO_2{}^+/NO_2$ couple,[43] but it is believed that $NO_2{}^+$ never reacts through an outer-sphere mechanism.[44,45] A very low self-exchange rate constant was reported for reduction of $S_2O_8{}^{2-}$ ($k \sim 10^{-18}$ M^{-1} s^{-1}), but this system is not really comparable with ours because O–O bond cleavage is most likely concerted with electron transfer.[46] Among coordination compounds, the following systems are notable: $[Co(NH_3)_6]^{3+/2+}$ ($k_{11} = 4 \times 10^{-6}$ M^{-1} s^{-1}),[47] $Cu^{2+/+}(aq)$ ($k_{11} = 5 \times 10^{-7}$ M^{-1} s^{-1}),[48] $[Cu(im)_n]^{2+/+}$ ($k_{11} = 1 \times 10^{-7}$ M^{-1} s^{-1}),[48] and $Cr^{3+/2+}(aq)$ ($k_{11} \sim 10^{-10}$ M^{-1} s^{-1}).[49] There is considerable uncertainty in the result cited for the $Cr^{3+/2+}(aq)$ system. Among organic systems, if those involving concerted bond cleavage are excluded, the *N*-bromosuccinimide$^{0/-}$ system appears to have the largest reorganizational energy yet reported, with $\lambda = 300$ kJ mol^{-1}.[50] In summary, the Marcus cross relationship leads to a self-exchange rate constant for the $NH_2OH^{+/0}$ redox couple that is lower by far than that for any other redox couple yet reported.

In order to obtain an independent assessment of the reorganizational energy, ab initio calculations were performed on NH_2OH and NH_2OH^+. To our knowledge, prior calculations on the cation have been performed only at the Hartree–Fock level.[51] Geometries were optimized for both molecules at

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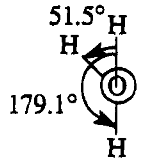
Table 2. Computed Geometries of NH_2OH, NH_2OH^+, and Self-Exchange Transition States

	r_{N-O}, Å	r_{O-H}, Å	r_{N-H}, Å	$\angle_{HNH}$, deg	$\angle_{HNO}$, deg	$\angle_{NOH}$, deg
			NH_2OH, C_s			
MP2/6-31+G(d)	1.455	0.973	1.021	106.4	103.2	101.9
MP2/6-311+G(d,p)	1.435	0.960	1.017	105.9	104.3	101.7
QCISD/6-311+G(d,p)	1.434	0.956	1.018	105.1	103.9	101.8
exp[a]	1.453	0.96	1.02	107.1	103.3	101.4
			NH_2OH^+, C_s Planar			
MP2/6-31+G(d)	1.296	0.993	1.022, 1.023	124.8	113.6, 121.6	110.8
MP2/6-311+G(d,p)	1.285	0.980	1.018, 1.020	124.4	114.0, 121.6	110.4
QCISD/6-311+G(d,p)	1.298	0.976	1.022, 1.020	124.2	114.0, 121.8	109.8
			C_1 Transition State			
MP2/6-31+G(d)	1.365	0.984	1.020, 1.026	113.7	107.3, 113.0	107.3
MP2/6-311+G(d,p)	1.351	0.971	1.016, 1.021	113.7	106.7, 113.0	107.0
						
			C_s Transition State			
MP2/6-31+G(d)	1.373	0.984	1.022	116.4	109.6	107.3
MP2/6-311+G(d,p)	1.358	0.971	1.018	116.8	112.7	106.9
			Structural Differences ($NH_2OH^+ - NH_2OH$) at the QCISD Level			
	−0.136	0.020	0.003, 0.002	19.1	10.1, 17.9	8.0

[a] Reference 53.

various levels, as shown in Table 2. In the case of NH_2OH, the ground state of the molecule is $^1A'$ in the C_s point group with the mirror plane bisecting the H−N−H bond angle and the O−H bond trans to this bond angle. The ground state of NH_2OH^+ is identified as $^2A''$, also in the C_s point group, but now with the whole molecule coplanar. As the geometric parameters listed in Table 2 show, the agreement between the calculations at the various levels of theory is sufficiently good that the results may be taken with confidence. Thus, ionization leads to major structural changes, including planarization at the nitrogen atom, shortening of the N−O bond by 0.136 Å, and rotation about the N−O bond by 90°.

With such drastic structural differences between NH_2OH and its radical cation, it was decided to locate the transition state geometry for the self-exchange reaction by use of ab initio methods rather than by use of a classical force field. Two transition state geometries were optimized at the MP2/6−311+G(d,p) level of theory. One of these was obtained with no symmetry constraints on the two molecules except that they have identical geometries. The outcome, as shown in Table 2, was a C_1 structure intermediate in geometry between the structures of the two reactants. An energy calculation at this geometry, but at the QCISD(T) level, gave a value of 414 kJ mol^{-1} for λ_i. An alternative transition state structure was investigated in which the molecular symmetry was constrained to the C_s point group, with the mirror plane including the OH bond and bisecting the NH_2 bond angle (as in the ground state of NH_2OH); this gave a value for λ_i of 409 kJ mol^{-1}. Apparently the energy of the transition state is not very sensitive to rotation of the OH group about the NO bond, so that a change in the level of theory leads to a small inversion in the energies. By analogy with related systems,[52] we may estimate a value of 120 kJ mol^{-1} for λ_o. Thus, the sum of λ_o and λ_i gives a value of ~530 kJ mol^{-1} for λ, which is in remarkably good agreement with that deduced by use of the Marcus cross relationship. In summary, the observed kinetics is in agreement with an outer-sphere electron transfer mechanism.

A rate constant of 12 M^{-1} s^{-1} was reported for the oxidation of NH_2OH by $[W(CN)_8]^{3-}$.[6] This is quite similar to the result we have obtained for the oxidation by $[IrCl_6]^{2-}$. However, $[W(CN)_8]^{3-}$ has a reduction potential of 0.57 V, which makes it 0.3 V weaker as an oxidant than $[IrCl_6]^{2-}$. One conceivable explanation for the similarity of the two rate constants is that trace metal catalysis resulted in spurious rates for the $[W(CN)_8]^{3-}$ system. The enormous Franck−Condon barrier associated with outer-sphere oxidation of NH_2OH may explain why such reactions are highly susceptible to various modes of catalysis, and it suggests that bona fide examples of outer-sphere oxidations of NH_2OH should occur only rarely.

Conclusions. The oxidation of NH_2OH by $[IrCl_6]^{2-}$ is catalyzed by trace levels of Cu^{2+}, Fe^{2+}, and hydrolyzed forms of the oxidant. When these paths are appropriately suppressed, the rate law is first order with respect to each reactant. An electron-transfer mechanism is inferred, with the first step being formation of the cation radical NH_2OH^+. A record-low self-exchange rate constant of 5×10^{-13} M^{-1} s^{-1} for the NH_2OH^+/NH_2OH redox couple is derived by use of the Marcus cross relationship, and it is supported by ab initio calculations.

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