Intermediates Produced from the One-Electron Oxidation and Reduction of Hydroxylamines. Acid–Base Properties of the Amino, Hydroxyamino, and Methoxyamino Radicals

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Abstract: The optical absorption spectra of the intermediates produced from the one-electron oxidation and reduction of hydroxylamines were observed using the technique of pulse radiolysis. The hydroxyl radicals produced from the radiolysis of water were found to react much faster with the unprotonated hydroxylamines as compared to the protonated form: $k(OH + N^+H_3OH) \leqslant 5.0 \times 10^8\ M^{-1}\ sec^{-1}$, $k(OH + NH_2OH) = 9.5 \times 10^9\ M^{-1}\ sec^{-1}$. The intermediate produced has an absorption maximum at 217 nm, $\epsilon_{217}\ 2.5 \times 10^3\ M^{-1}\ cm^{-1}$, and decays by second-order kinetics, $2k = 4.5 \pm 2.0 \times 10^8\ M^{-1}\ sec^{-1}$. This spectrum is assigned to the hydroxylamino radical $\cdot NHOH$. From an examination of its acid–base properties, a $pK(\cdot N^+H_2OH \rightleftharpoons \cdot NHOH + H^+) = 4.2 \pm 0.1$ was obtained. A similar examination of the one-electron oxidation of *O*-methylhydroxylamine shows λ_{max} 218 nm, $\epsilon_{218}\ 1.4 \times 10^3\ M^{-1}\ cm^{-1}$, $2k = 1.4 \times 10^9\ M^{-1}\ cm^{-1}$, and $pK(\cdot N^+H_2OCH_3 \rightleftharpoons \cdot NHOCH_3 + H^+) = 2.9 \pm 0.2$. One-electron reduction of hydroxylamine by hydrated electrons showed a dependence on the state of protonation of the molecule: $k(e_{aq}^- + N^+H_3OH) = 1.2 \times 10^{10}\ M^{-1}\ sec^{-1}$ and $k(e_{aq}^- + NH_2OH) = 9.2 \times 10^8\ M^{-1}\ sec^{-1}$. The intermediate produced is the ammonium radical cation, $e_{aq}^- + N^+H_3OH \rightarrow \cdot NH_3^+ + OH^-$, and its adduct to benzene to give the $NH_2C_6H_6$ radical has λ_{max} 310 nm and ϵ_{310} 7400 $M^{-1}\ cm^{-1}$. A similar reaction takes place with *O*-methylhydroxylamine. From its pH dependence on reaction with thiocyanate ions, the dissociation constant of the ammonium radical cation was obtained, $pK(\cdot NH_3^+ \rightleftharpoons \cdot NH_2 + H^+) = 6.7 \pm 0.2$. The properties of this radical are discussed.

The chemical properties of hydroxylamine indicate that it can be readily reduced *and* readily oxidized. Reduction of hydroxylamine usually gives ammonia as an end product, while oxidation gives nitrogen and various nitrogen oxides depending on the system and the experimental conditions. Hydroxylamine is also *formed* in biological processes from both oxidative and reductive methods.

The oxidation of hydroxylamine by ceric sulfate[2] and by ferricyanide[3] in acidic solutions has been studied in detail. The kinetics of the oxidation were found to be dependent upon both the pH and the concentration of both components. Formation of a complex with cerium(IV) has been suggested and the $NH_2O\cdot$ radical has been postulated[2b,c] as an intermediate. Reduction of NH_2OH by titanium(III) ions has been shown[4] to produce the amino radical $\cdot NH_2$. The radiation chemistry of hydroxylamine in aqueous solution has been studied;[5] the main products determined were ammonia and nitrogen.

In this work, the optical absorption spectra, extinction coefficients, decay kinetics, and dissociation constants of the intermediates produced from the one-electron oxidation (by OH radicals) and one-electron reduction (by e_{aq}^-) of hydroxylamines have been determined. The techniques of pulse radiolysis and kinetic absorption spectrophotometry were used to observe and study these transient species.

Experimental Section

A Febetron 705 (Field Emission Corp.) pulsed-radiation source was used to produce single pulses of ~30 nsec of 2.3-MeV electrons. These electrons were absorbed by the aqueous solution contained in quartz optical cells of 2-cm optical path. A double monochromator was used to reduce scattered light below 260 nm, and the 450-W Xenon lamp was pulsed for short durations to increase the light output by a factor of ~20. Full details of the experimental conditions have been described elsewhere.[6]

The water used was purified[6] by triplet distillation, irradiation, and photolysis. Reagent grade hydroxylamine sulfate was supplied by Baker and Adamson, *O*-methylhydroxylamine chloride by J. T. Baker, *N*-methylhydroxylamine chloride and *N,N*-diethylhydroxylamine by Aldrich.

Absorbances were measured $\leqslant 0.5$ µsec after the electron pulse, and the dosimetry used was 0.1 *M* KCNS. The extinction coefficients were derived taking $G(e_{aq}^-) = G(OH) = 2.8$. The pH was adjusted with perchloric acid and potassium hydroxide, and the solutions were buffered with borate (~2 m*M*) and phosphate (~2 m*M*) or were self-buffered. All experiments were carried out at room temperature (~22°).

Results

The radiation chemistry of water and aqueous solutions is known to produce OH radicals, H atoms, and hydrated electrons, in addition to molecular hydrogen and hydrogen peroxide

$$H_2O \rightsquigarrow OH\ (2.8),\ H\ (0.55),\ e_{aq}^-\ (2.8),\ H_2\ (0.45),\ H_2O_2\ (0.71)$$

where the numbers in parentheses are the *G* values, *i.e.*, the yields produced per 100 eV of energy absorbed. In order to study the reactions of OH radicals in the absence of e_{aq}^-, the latter were converted into OH radicals by saturating (1 atm = 2.5×10^{-2} *M*) the

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(1) National Academy of Science–National Research Council Research Associate at Natick.

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Table I. Rates of Reaction of e_{aq}^- and OH Radicals with Hydroxylamines in Aqueous Solution

Solute	Form	$k(e_{aq}^- + S)$, M^{-1} sec^{-1}	$k(OH \times S)$, M^{-1} sec^{-1} [a]
Hydroxylamine	N^+H_3OH	1.2×10^{10} (pH 4.8)	$\leqslant 5.0 \times 10^8$ (pH 4.0)[b]
	NH_2OH	9.2×10^8 (pH 9.0)	9.5×10^9 (pH 8.0)
O-Methylhydroxylamine	$N^+H_3OCH_3$	$\geqslant 1.9 \times 10^{10}$ (pH 4.5)[b]	$\leqslant 4.0 \times 10^8$ (pH 4.5)[b]
	NH_2OCH_3	4.4×10^8 (pH 9.1)	1.4×10^{10} (pH 9.1)
N-Methylhydroxylamine	$CH_3N^+H_2OH$	1.3×10^{10} (pH 4.8)	
	CH_3NHOH	2.4×10^8 (pH 9.0)	
N,*N*-Diethylhydroxylamine	$(C_2H_5)_2N^+HOH$	$\geqslant 1.2 \times 10^{10}$ (pH 4.7)[b]	
	$(C_2H_5)_2NOH$	2.4×10^8 (pH 9.1)	

[a] Rate constant values to ±10%, determined *vs.* KCNS, taking $k(OH + CNS^-) = 1.1 \times 10^{10}$ M^{-1} sec^{-1}. [b] Owing to the p*K* values of the parent molecules, these determined rate values could be somewhat higher (*e.g.*, ~30% higher for $N^+H_3OCH_3$).

solution with nitrous oxide

$$e_{aq}^- + N_2O \longrightarrow N_2 + OH + OH^- \qquad (1)$$

where $k_1 = 5.6 \times 10^9$ M^{-1} sec^{-1}.[7]

The absolute rates of reaction of e_{aq}^- with hydroxylamine, *O*-methylhydroxylamine, *N*-methylhydroxylamine, and *N*,*N*-diethylhydroxylamine were determined by following the decay kinetics of e_{aq}^- at 700 nm. These rates were determined at two pH values to have the protonated or the unprotonated hydroxylamine forms present in solution. These rates are given in Table I. The hydroxylamines studied have the following dissociation constants: p$K(NH_2OH) = 6.08$,[8] p$K(NH_2OCH_3) = 4.6$,[9] p$K(CH_3NHOH) = 4.75$,[9] and p$K[(C_2H_5)_2NOH] \geq 4.8$. It can be seen from Table I that these rates are markedly dependent on the state of protonation of the hydroxylamine. Protonated hydroxylamines react with e_{aq}^- with rates which are almost diffusion controlled, *e.g.*, $k(e_{aq}^- + N^+H_3OH) = 1.2 \times 10^{10}$ M^{-1} sec^{-1}. The reactivity of e_{aq}^- with unprotonated hydroxylamines is 10–50 times lower, depending on the nature of the hydroxylamine derivative.[10] The electron-withdrawing power of the –OH group reduces the electron-donating power of the nitrogen, and hence $k(e_{aq}^- + NH_2OH) = 9.2 \times 10^8$ M^{-1} sec^{-1} compared to $k(e_{aq}^- + NH_2OCH_3) = 4.4 \times 10^8$ M^{-1} sec^{-1}.

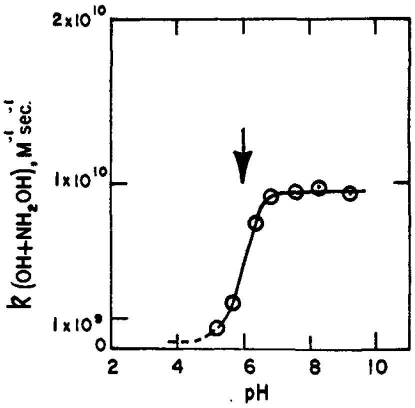

Figure 1. Dependence upon pH of the rate constant for the reaction of OH radicals with hydroxylamine. Absolute rate derived using the thiocyanate method, taking $k(OH + CNS^-) = 1.1 \times 10^{10}$ M^{-1} sec^{-1}.

As expected from the electrophilic properties of the OH radical, the rates of reaction of hydroxylamines with OH radicals follow exactly the opposite course. These rates were determined *vs.* CNS^- by following the diminution of $(CNS)_2\cdot^-$ at 500 nm in the presence of various concentrations of hydroxylamine, and taking[11] $k(OH + CNS^-) = 1.1 \times 10^{10}$ M^{-1} sec^{-1}. The rates are high with unprotonated hydroxylamines, and lower with protonated hydroxylamines. Figure 1 shows this pH dependence, and the rates are given in Table I. It is interesting to note that from Figure 1 one can derive the p$K(NH_2OH) = 6.0 \pm 0.1$, in excellent agreement with the literature value. Similar dependence of the rates of reaction of OH radicals with aliphatic amines[12] and hydrazine[13] have recently been observed.

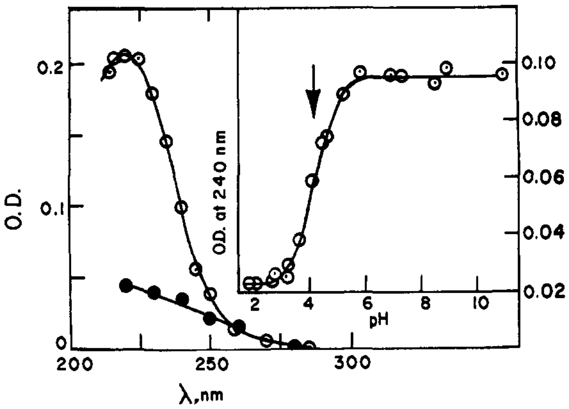

Figure 2. Absorption spectra of intermediates produced from the reaction of OH radicals with NH_2OH. Experiment carried out in the presence of N_2O (1 atm) using 2 m*M* NH_2OH at pH 6.4, ○, and 20 m*M* NH_2OH at pH 3.0, ●. Total dose = 8.0 krads/pulse. Insert: OD_{240} *vs.* pH curve of intermediate (50 m*M* NH_2OH at pH <4.2 in argon, and 5 m*M* NH_2OH at pH >4.2 in N_2O were used).

Oxidation. The one-electron oxidation of hydroxylamine by OH radicals produces intermediates which absorb in the far-ultraviolet region of the spectrum; Figure 2. Solutions of hydroxylamine were saturated with N_2O, and the concentration was chosen such that all the e_{aq}^- reacted with N_2O and all the OH radicals

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Table II. Absorption Maxima, Extinction Coefficients, Decay Kinetics, and pK Values of Intermediates Produced from the Reaction of OH Radicals with Hydroxylamines

Solute	pH	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	$2k$, M^{-1} sec^{-1}	Suggested radical	pK Radical	pK Solute
Hydroxylamine	6.4	217	2.5×10^3	4.5×10^8 [a]	$\cdot NHOH$		
					$\downarrow\uparrow$	4.2 ± 0.1	6.0 ± 0.1
	3.2	<220	6×10^2 [b]		$\cdot N^+H_2OH$		
O-Methyl-hydroxylamine	5.7	218	1.4×10^3	1.4×10^9	$\cdot NHOCH_3$		
					$\downarrow\uparrow$	2.9 ± 0.2	4.6
	1.7	<220	2.8×10^2 [b]		$\cdot N^+H_2OCH_3$		

[a] The decay of ·NHOH radicals is not a perfect second-order process. [b] At 220 nm.

with NH_2OH, under the conditions of the experiment. A transient spectrum with λ_{max} 217 nm and ϵ_{217} 2.5×10^3 M^{-1} cm^{-1} was obtained at pH 6.4, which remained unchanged up to pH ~11.0. Owing to the alkaline hydrolysis of NH_2OH, the solutions were degassed and made alkaline immediately prior to pulse radiolysis. In acid solution, a weak absorption with a maximum below 220 nm is observed. The acid-base property of this radical was determined by monitoring the change in absorbance with pH at 240 nm. From this curve (see Figure 2) a $pK = 4.2 \pm 0.1$ was obtained.

The one-electron oxidation of *O*-methylhydroxylamine by OH radicals produces a similar intermediate, with λ_{max} ~218 nm and ϵ_{218} 1.4×10^3 M^{-1} sec^{-1}, at pH 5.7; see Figure 3. By monitoring at 235 nm the change in absorbance with pH, a $pK = 2.9 \pm 0.2$ was obtained from the dissociation constant of this intermediate. The hydrochloride salt of NH_2OCH_3 used does not affect the primary reactions taking place, since even at pH 2 the rate $k(OH + Cl^-) = 4 \times 10^7$ M^{-1} sec^{-1} (ref 7) and therefore all the OH radicals react with NH_2OCH_3.

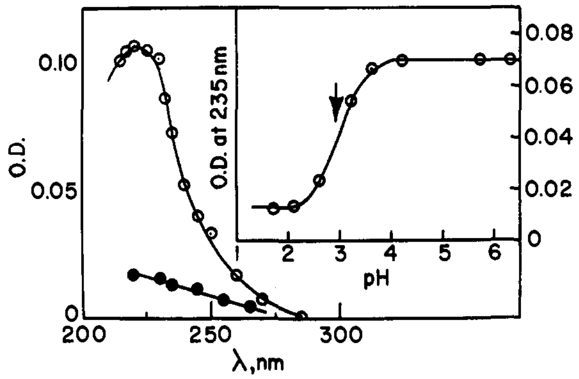

Figure 3. Absorption spectra of intermediates produced from the reaction of OH radicals with NH_2OCH_3. Experiment carried out in the presence of N_2O (1 atm) using 5 m*M* NH_2OCH_3 at pH 5.7, ○, and 50 m*M* NH_2OCH_3 at pH 1.7, ●. Total dose ~ 4.0 krads/pulse. Insert: OD_{235} *vs.* pH curve of intermediate (50 m*M* NH_2OCH_3 at pH <3.2 and 5 m*M* NH_2OCH_3 at pH >3.2).

The radicals produced from the oxidation of NH_2OH and NH_2OCH_3 decay by a second-order process; see Table II.

Reduction. The one-electron reduction by e_{aq}^- of hydroxylamine produces an oxidizing equivalent: the amino $\cdot NH_2$ radical or the OH radical

$$N^+H_3OH + e_{aq}^- \longrightarrow \cdot N^+H_3 + OH^- \quad (2)$$

$$NH_2OH + e_{aq}^- \longrightarrow \cdot NH_2 + OH^- \quad (3)$$

where $k_2 = 1.2 \times 10^{10}$ M^{-1} sec^{-1} and $k_3 = 9.2 \times 10^8$ M^{-1} sec^{-1}. The absorption spectrum of $\cdot NH_2$ radical has been observed in the flash photolysis of gaseous ammonia,[14] and the esr spectra of NH_2 trapped in solid rare gas matrices at 4.2°K[15] or in X-irradiated NH_4ClO_4[16] crystals have been examined. No transient that could be assigned to the $\cdot NH_2$ or $\cdot NH_3^+$ radical was observed on pulse radiolysis of air-free 5 m*M* NH_2OH at pH 7.0 or 3.0. This is not surprising in view of the recently reported[17] weak spectrum of the NH_2 radical produced on pulse radiolysis of an aqueous solution of ammonia with λ_{max} 525 nm and ϵ_{525} 75 M^{-1} cm^{-1}. Under our experimental conditions it would not be possible to detect such a weak transient absorption. Furthermore, the $\cdot NH_2$ radical would decay rapidly by reaction with hydroxylamine (see more below).

In order to establish the formation of the amino radical by the reactions of e_{aq}^- with hydroxylamine, and to disprove the thermodynamically less probable reaction, $N^+H_3OH + e_{aq}^- \rightarrow NH_3 + OH\cdot$, the adducts of OH radicals and of the species formed by the reaction with e_{aq}^- were investigated. Figure 4 shows the transient absorption spectra produced in the pulse radiolysis of aqueous solutions of (a) 20 m*M* benzene, saturated with N_2O (1 atm) at pH 3.3 [Under these conditions, only the OH radical adduct to benzene is produced. This transient, $OH\dot{C}_6H_6$, has absorption maxima at 314, 297, and 283 nm with ϵ_{314} 4900 M^{-1} cm^{-1}, ϵ_{297} 4250 M^{-1} cm^{-1}, and ϵ_{283} 3600 M^{-1} cm^{-1}. Dorfman, *et al.*,[18] have reported a λ_{max} 313 nm and ϵ_{313} 3500 ± 800 M^{-1} cm^{-1} for this radical. The $OH\dot{C}_6H_6$ radical decays with $2k = 4.2 \times 10^9$ M^{-1} sec^{-1}.]; (b) 20 m*M* benzene, 5 m*M* NH_2OH Ar (1 atm), pH 3.65 [Under these conditions all the OH radicals produce $OH\dot{C}_6H_6$ and all the e_{aq}^-'s react with N^+H_3OH. It is seen (Figure 4) that the overall transient spectrum is quite different from that of $OH\dot{C}_6H_6$ radicals. By subtraction of the portion of the spectrum due to $OH\dot{C}_6H_6$, a spectrum with λ_{max} 310 nm and ϵ_{310} 7400 M^{-1} cm^{-1} is obtained. This spectrum is assigned to the $NH_2\dot{C}_6H_6$ radical (or $N^+H_3\dot{C}_6H_6$; reference will be made to the former form).]; (c) 10 m*M* benzene, 10 m*M* NH_2OH, 1.0 *M* *tert*-BuOH, Ar(1 atm), pH 3.6. Under these conditions, all the OH radicals react with *tert*-

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BuOH, producing the $\dot{C}H_2C(CH_3)_2OH$ radical which absorbs at λ_{max} 225 nm (ref 6a), and all the e_{aq}^-'s react with N^+H_3OH. The transient spectrum has λ_{max} 310 nm, ϵ_{310} 7400 M^{-1} cm^{-1} and is identical with that produced above. The amino radical appears to react relatively slowly with *tert*-BuOH. The formation of the $NH_2\dot{C}_6H_6$ radical supports the mechanism suggested in reactions 2 and 3. It is interesting to note that at pH 9.0 the $NH_2\dot{C}_6H_6$ radical was not observed. At this pH, the amino radical is in the form $\cdot NH_2$ (see more below) and apparently does not add to benzene.

Discussion

The one-electron oxidation of hydroxylamine could produce the $NH_2O\cdot$ or the $\cdot NHOH$ radicals as intermediates. The $NH_2O\cdot$ radical has been postulated in the oxidation mechanism of hydroxylamine by Ce(IV)[2] and ferricyanide ions.[3] The hydroxylamino radical has been suggested by Lefort and Tarrago[5] in the radiation chemistry of aqueous solutions of hydroxylamine, and by Abel[19] in the autodecomposition of NH_2OH. No direct observation or identification of the hydroxylamino radical has been reported. The similarity in the transient absorption of the intermediates produced from the reaction of OH radicals with NH_2OH and NH_2OCH_3, but the significant difference in the acid–base properties of these radicals (see Figures 2 and 3), strongly suggests that the transient species observed are due to $\cdot N^+H_2OH$, $\cdot NHOH$ and to $\cdot N^+H_2OCH_3$, $\cdot NHOCH_3$

$$OH + NH_2OH \longrightarrow \cdot NHOH + H_2O \qquad (4)$$

$$OH + \overset{+}{N}H_3OH \longrightarrow \cdot\overset{+}{N}H_2OH + H_2O \qquad (5)$$

$$\cdot\overset{+}{N}H_2OH \xrightleftharpoons{pK\ 4.2 \pm 0.1} \cdot NHOH + H^+ \qquad (6)$$

and for *O*-methylhydroxylamine

$$OH + NH_2OCH_3 \longrightarrow \cdot NHOCH_3 + H_2O \qquad (7)$$

$$OH + \overset{+}{N}H_3OCH_3 \longrightarrow \cdot\overset{+}{N}H_2OCH_3 + H_2O \qquad (8)$$

$$\cdot\overset{+}{N}H_2OCH_3 \xrightleftharpoons{pK\ =\ 2.9 \pm 0.2} \cdot NHOCH_3 + H^+ \qquad (9)$$

Some OH radical attack on the methyl group cannot be excluded.

Since pK(NH_2OH) = 6.1 ± 0.1 and pK(NH_2OCH_3) = 4.6 ± 0.1, one would expect a change in the same direction for the dissocation constants of the $\cdot N^+H_2OH$ and $\cdot N^+H_2OCH_3$ radicals. These differences are indeed observed (Figures 2 and 3) and pK($\cdot N^+H_2OH$) = 4.2 ± 0.1 and pK($\cdot N^+H_2OCH_3$) = 2.9 ± 0.2 have been determined. The strong pH dependence of the reaction of OH radicals with these hyroxylamines (Figure 1 and Table I) supports the conclusion that the center of attack by OH radicals is on the nitrogen.

Results similar to those shown in Figure 2 have recently been obtained by Behar, Shapira, and Treinin[20] in the pulse radiolysis and flash photolysis of aqueous solutions of hydroxylamine.

At pH 6–7, Lefort and Tarrago[5] found $G(NH_3)$ = 2.7, $G(N_2)$ = 2.7, $G(H_2O_2)$ = 0.4, and $G(-NH_2OH)$ = 8.1 in the radiation chemistry of air-free aqueous solutions of hydroxylamine. In addition to reactions 2–5, at pH 6–7 the hydroxylamino radical is present as $\dot{N}HOH$ and the amino radical has a pK ~ 6.7 ± 0.2 (see below). The following reactions are suggested.

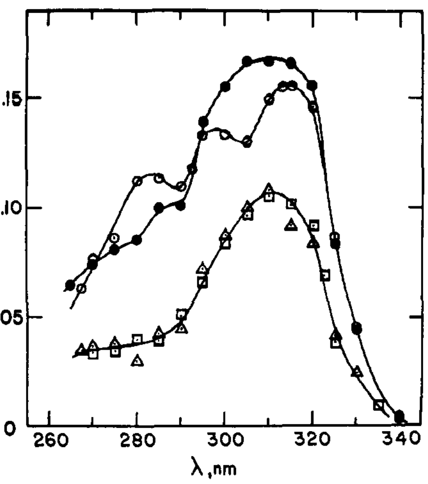

Figure 4. Absorption spectra of the $NH_3\cdot^+$ and $OH\cdot$ radical adducts to benzene. The $C_6H_6OH\cdot$ radical, ○, was produced from the pulse radiolysis of 20 mM benzene in N_2O (1 atm) at pH 3.3; the $C_6H_6NH_2\cdot$ radical, □, was produced from the pulse radiolysis of 10 mM benzene, 10 mM NH_2OH, and 1.0 M *tert*-BuOH at pH 3.6 in Ar (1 atm). Equimolar mixtures of $C_6H_6OH\cdot$ and $C_6H_6NH_2\cdot$ radicals were produced in 20 mM benzene and 5 mM NH_2OH at pH 3.65 in Ar (1 atm) solution, ●. The symbol △ represents (● − ½○) and gives the spectrum of the $C_6H_6NH_2\cdot$ radical. Total dose ~2.5 krads/pulse.

$$\cdot NH_2 + \overset{+}{N}H_3OH \longrightarrow NH_3 + \cdot NHOH + H^+ \qquad (10)$$

$$\cdot\overset{+}{N}H_3 + NH_2OH \longrightarrow NH_3 + \cdot NHOH + H^+ \qquad (11)$$

$$2\cdot NHOH \longrightarrow [HOHN\text{–}NHOH] \longrightarrow N_2 + 2H_2O \qquad (12)$$

Stoichiometrically, all the amino radicals react with hydroxylamine to produce NH_3 (actually NH_4^+) and $\dot{N}HOH$ radicals. Hence

$$G(N_2) = (1/2)[G(e_{aq}^-) + G(OH)]$$

$$G(NH_3) = G(e_{aq}^-)$$

In acidic solutions, no H_2O_2 was observed.[5] Since no thermal reaction occurred[5] under these conditions, the decomposition is probably due to reaction 13.

$$\cdot\overset{+}{N}H_2OH + H_2O_2 \longrightarrow \dot{N}OH + OH + H^+ + H_2O \qquad (13)$$

$$2\dot{N}OH \rightleftharpoons N_2O_2H_2 \longrightarrow N_2O + H_2O \qquad (14)$$

The corresponding reaction 15 is probably much slower.

$$\dot{N}HOH + H_2O_2 \longrightarrow \dot{N}OH + OH + H_2O \qquad (15)$$

The properties of the nitroxyl radical are currently under study.[21]

The observation of the esr spectrum[2] of $NH_2O\cdot$ radicals in acidic solutions of Ce^{4+} ions and hydroxylamine could be due to: (a) complexation and the production of a different intermediate, (b) the primarily produced $\cdot N^+H_2OH$ radical undergoing tautomerization in acidic solutions to the $NH_2O\cdot$ radical, or (c) the $\cdot N^+H_2OH$ radical reacting with N^+H_3OH to give the $NH_2O\cdot$ radical. Present results cannot distinguish among these possibilities. None of these reactions could occur with *O*-methylhydroxylamine. The assignment of the spectra observed in Figures 2 and 3 and the pK of the radicals remain unaffected.

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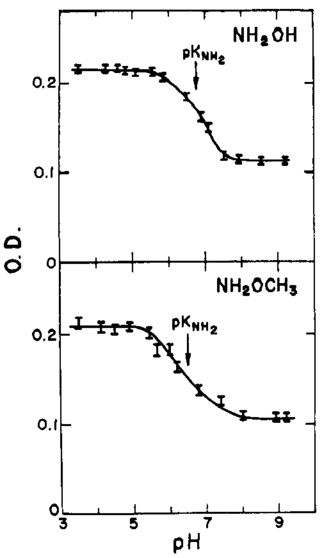

Figure 5. Derivation of the pK of the $NH_2\cdot$ radical (see text for the method used). The $NH_2\cdot$ radical is produced from the one-electron reduction of NH_2OH (top curve) and NH_2OCH_3 (bottom curve).

The one-electron reduction of hydroxylamine by e_{aq}^- is suggested to lead to the formation of the amino radical; reactions 2 and 3. A $G(e_{aq}^-) = G(NH_3) = 2.7$ in the radiolysis[5] of air-free hydroxylamine at pH 6–7 supports this mechanism. The $\cdot N^+H_3$ radical adduct to benzene was observed (Figure 4) and is in support of this reaction. Direct observation of the ammonium radical cation was not possible under our experimental conditions. It was, however, accidently found that the $\cdot NH_3^+$ radical reacts with CNS^- ions to produce $CNS\cdot$ radicals

$$\cdot\overset{+}{N}H_3 + CNS^- \longrightarrow NH_3 + \cdot CNS \qquad (16)$$

$$\cdot CNS + CNS^- \longrightarrow \cdot(CNS)_2^- \qquad (17)$$

while the neutral amino radical $\cdot NH_2$ produced at higher pH values apparently does not react with CNS^- ions. The $(CNS)_2^-$ radical anion[22] has an absorption maximum at 500 nm and ϵ_{580} 7100 M^{-1} cm^{-1}. The acid–base properties and the dissociation constant of the ammonium radical cation were therefore determined by following the change in absorbance of $(CNS)_2^-$ at 500 nm as a function of pH. Pulse radiolysis of argon-saturated aqueous solutions of 0.2 M KCNS and 10^{-2} M NH_2OH (or 10^{-2} M NH_2OCH_3) were examined. Under these conditions, all the OH radical reacted with CNS^- ions and all the e_{aq}^- with NH_2OH or N^+H_3OH. Figure 5 shows the results obtained for NH_2OH and NH_2OCH_3. These results show (a) that the yield of $(CNS)_2^-$ doubles when reaction 16 takes place [this is in keeping with $G[(\cdot CNS)_2^-]$ being equal to $G(OH)$ at high pH (>8) or to $G(OH) + G(e_{aq}^-)$ at low pH (<4)], (b) that the pK of the ammonium radical cation is (within experimental error) the same in solutions of NH_2OH or NH_2OCH_3 (the reaction of e_{aq}^- with NH_2OCH_3 is also expected to lead to the formation of amino radicals, *e.g.*, eq 18 and 19), and (c) that the pK values for the acid–base

$$e_{aq}^- + \overset{+}{N}H_3OCH_3 \longrightarrow \cdot\overset{+}{N}H_3 + CH_3O^- \qquad (18)$$

$$e_{aq}^- + NH_2OCH_3 \longrightarrow \cdot NH_2 + CH_3O^- \qquad (19)$$

equilibrium (eq 20) of the amino radical are in good agreement.

$$\cdot\overset{+}{N}H_3 \overset{pK\ 6.7 \pm 0.2}{\rightleftharpoons} \dot{N}H_2 + H^+ \qquad (20)$$

Although the OH and the NH_2 radicals are isoelectronic, their reactions can be considerably different. This probably arises from the considerably lower electrophilic nature of the NH_2 radical. Transfer of an electron from CNS^- ions to NH_2 is not probable, while $k(OH + CNS^- \rightarrow \cdot CNS + OH^-) = 1.1 \pm 10^{10}$ M^{-1} sec^{-1}. Similarly, the addition of the NH_2 radical to the benzene ring does not occur.

The electrophilic nature of the amino radical is greatly increased when protonated (see also ref 23 and references cited therein). The $\cdot NH_3^+$ radical can now undergo an electron-transfer reaction with CNS^- ions and add to the benzene ring. Its reactivity probably approaches that of the OH radical.

It is interesting to compare some pK values for water and ammonia, as well as for the corresponding oxidizing radicals.

$$pK(H_2O \rightleftharpoons H^+ + OH^-) = 15.7$$

$$pK(NH_3 \rightleftharpoons H^+ + NH_2^-) \sim 33$$

$$pK(H_3O^+ \rightleftharpoons H^+ + H_2O) = -1.7$$

$$pK(NH_4^+ \rightleftharpoons H^+ + NH_3) = 9.24$$

$$pK(H_2O^+ \rightleftharpoons H^+ + OH) = ?$$

$$pK(NH_3^+ \rightleftharpoons H^+ + NH_2) = 6.7$$

$$pK(OH \rightleftharpoons O\cdot^- + H^+) = 11.9$$

$$pK(NH_2 \rightleftharpoons H^+ + NH^-) = ?$$

From these simple analogies, $pK(H_2O^+ \rightleftharpoons H^+ + OH)$ is probably well below zero and $pK(NH_2 \rightleftharpoons H^+ + NH^-)$ is probably well above 11.9.

Finally, it is interesting to note the differences in the dissociation constants of the amino ($pK_{\cdot N^+H_3} = 6.7$), hydroxyamino ($pK_{\cdot N^+H_2OH} = 4.2$), and methoxyamino ($pK_{\cdot N^+H_2OCH_3} = 2.9$) radicals. The electron-withdrawing power of the –OH and –OCH_3 groups affects the dissociation constant of the corresponding radicals just as well. Indeed the ratio of the dissociation constant of the parent compound to that of its corresponding radical is 1.5 ± 0.1 for NH_4^+, N^+H_3OH, and $N^+H_3OCH_3$.

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[23] C. J. Micheyada and W. P. Hoss, *J. Amer. Chem. Soc.*, **92**, 6298 (1970); W. C. Danen and T. T. Kensler, *ibid.*, **92**, 5235 (1970).