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Radiolytic Reactions of Monochloramine in Aqueous Solutions

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Monochloramine reacts with hydrated electrons very rapidly, $k(\mathrm{NH_2Cl}+\mathrm{e_{aq}}^-) = (2.2 \pm 0.3) \times 10^{10}$ L mol^{-1} s^{-1}, to produce $^\bullet\mathrm{NH_2}$ radicals. It reacts with $^\bullet$OH radicals more slowly, $k(\mathrm{NH_2Cl}+{}^\bullet\mathrm{OH}) = (5.2 \pm 0.6) \times 10^8$ L mol^{-1} s^{-1}, to produce $^\bullet$NHCl radicals. While $^\bullet\mathrm{NH_2}$ exhibits an absorption peak at 530 nm, with a molar absorption coefficient $\epsilon_{530} = 80$ L mol^{-1} cm^{-1}, $^\bullet$NHCl exhibits two peaks at 330 and 580 nm, $\epsilon_{330} = (85 \pm 30)$ L mol^{-1} cm^{-1} and $\epsilon_{580} = (56 \pm 30)$ L mol^{-1} cm^{-1}. The $^\bullet$NHCl radical undergoes self-decay and can react also with O_2 to form a peroxyl radical. It is suggested that the peroxyl radical exists in equilibrium $\mathrm{NHClO_2}^\bullet \leftrightarrows {}^\bullet\mathrm{NHCl} + \mathrm{O_2}$ with an estimated equilibrium constant of $(3 \pm 2) \times 10^{-3}$ mol L^{-1}. The reaction of chloramine with the carbonate radical is suggested to form a complex $[\mathrm{CO_3NH_2Cl}]^{\bullet-}$ with $k_\mathrm{f} = 2.5 \times 10^5$ L mol^{-1} s^{-1} and $k_\mathrm{r} = 4 \times 10^2$ s^{-1}, and this complex decomposes with $k = 7 \times 10^2$ s^{-1} to form $^\bullet$NHCl.

Introduction

Residual chlorine in discharged chlorinated water, e.g. cooling water from power plants, is toxic to aquatic life. In the presence of ammonia (0.07 to 4 μmol L^{-1} in seawater), chloramine is formed.[1−4]

$$\mathrm{Cl_2 + H_2O \leftrightarrows HOCl + H^+ + Cl^-} \tag{1}$$

$$\mathrm{NH_3 + HOCl \leftrightarrows NH_2Cl + H_2O} \tag{2}$$

Reaction 2 goes to equilibrium very rapidly and its equilibrium constant is very high[1−4] ($K_2 = 3.8 \times 10^{10}$ L mol^{-1}).[5] Chloramine is a relatively stable oxidant and toxic at low levels (4 μmol L^{-1}) to certain species of fish.[6] Chloramine is also used as a secondary weak disinfectant in water distribution systems.[7,8] It disappears from the system either by autodecomposition[9,10] or by autocatalytic reduction.[11,12] The autocatalytic mechanism was investigated in the presence of Fe(II) and was suggested to involve formation of the $^\bullet\mathrm{NH_2}$ radical as intermediate.[11,12] This radical is a strong oxidant, $E°(\mathrm{H^+},{}^\bullet\mathrm{NH_2}/\mathrm{NH_3}) = 2.3$ V,[13] and may itself oxidize chloramine.

Water may be purified by Advanced Oxidation Technologies (AOT) to remove organic materials. These processes involve radical reactions and the presence of chloramine in the water may have an effect on these radical reactions. The radical reactions of chloramines are important also in atmospheric chemistry. Chloramines may be formed in atmospheric droplets by reaction of chlorine, water, and ammonia via reactions 1 and 2. At pH <5 monochloramine disproportionates to form dichloramine and, at lower pH, trichloramine.

$$\mathrm{2NH_2Cl + H^+ \rightarrow NH_4^+ + NHCl_2} \tag{3}$$

$$\mathrm{2NHCl_2 + H^+ \rightarrow NH_3Cl^+ + NCl_3} \tag{4}$$

$$\mathrm{NH_3Cl^+ + NHCl_2 \rightarrow NH_4^+ + NCl_3} \tag{5}$$

Reactions 3−5 are general acid-catalyzed processes.[11,12] The chloramines can react with various radicals that may be present in atmospheric droplets or may be produced by AOT, e.g. $^\bullet$OH, $\mathrm{NO_3}^\bullet$, $\mathrm{SO_3}^{\bullet-}$, $\mathrm{SO_4}^{\bullet-}$, $\mathrm{SO_5}^{\bullet-}$, and $\mathrm{CO_3}^{\bullet-}$. To evaluate the effect of monochloramine on the decomposition of organic materials in water by AOT, the rate constants for reactions of monochloramine with the primary radicals of water radiolysis were determined.[14] The rate constants for reactions of $\mathrm{NH_2Cl}$ were reported to be $k(\mathrm{e_{aq}}^-) = 2.2 \times 10^{10}$ L mol^{-1} s^{-1}, $k(\mathrm{H}) = 1.2 \times 10^9$ L mol^{-1} s^{-1}, and $k(\mathrm{OH}) = 2.8 \times 10^9$ L mol^{-1} s^{-1}. To further elucidate the nature of these reactions and measure these and other rate constants we have carried out pulse radiolysis studies with monochloramine in aqueous solutions under various conditions.

Experimental Section[15]

The compounds used were analytical grade reagents from various sources: $\mathrm{NH_4Cl}$ (Aldrich), $\mathrm{(NH_4)_2SO_4}$ (Fisher), NaOCl (10% Cl, Mallinckrodt), $\mathrm{NaHCO_3}$ (Fisher), $\mathrm{Na_2CO_3}$ (Mallinckrodt), $\mathrm{C_6H_5CO_2H}$ (Aldrich), $\mathrm{Na_2B_4O_7}$ (Aldrich), and NaOH (50% w/w, Fisher). Water was purified with a Millipore Super-Q system. Fresh solutions of $\mathrm{NH_2Cl}$ were prepared from $\mathrm{NH_4Cl}$ and NaOCl ($1.5 > \mathrm{NH_4Cl/NaOCl} > 1$) at pH ≈9 (5 to 10 mmol L^{-1}) and were used within 8 h. The concentrations of $\mathrm{NH_2Cl}$ and $\mathrm{ClO^-}$ in the mixture were determined spectrophotometrically before each experiment (Figure 1), taking $\epsilon_{244} = 4.6 \times 10^2$ L mol^{-1} cm^{-1} for $\mathrm{NH_2Cl}$,[7,16] and $\epsilon_{292} = 3.5 \times 10^2$ L mol^{-1} cm^{-1} for $\mathrm{ClO^-}$.[17] In all experiments $[\mathrm{ClO^-}] < 0.01[\mathrm{NH_2Cl}]$. The concentration of $\mathrm{NHCl_2}$ under these conditions is negligible.[18] Sodium tetraborate was used as buffer to keep the pH near 9. Highly concentrated solutions of NaOH (free of carbonate) were used to increase the pH. In experiments with added carbonate, the pH was adjusted by mixing different proportions of $\mathrm{NaHCO_3}$ and $\mathrm{Na_2CO_3}$. Solutions were irradiated after saturation with N_2 or N_2O. To study the reactions of radicals with O_2, solutions were saturated with a mixture of N_2O/O_2. The gas mixture was prepared in a flow system by mixing N_2O and O_2. The ratio N_2O/O_2 was varied from 1:1 to 1:4. Pulse radiolysis experiments were carried out with the Linac-based apparatus described

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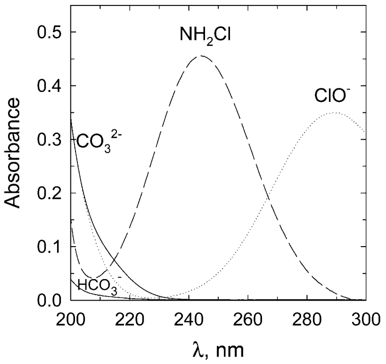

Figure 1. Optical absorption spectra of chloramine (pH 9), hypochlorite (pH 9), carbonate (pH 10.8), and bicarbonate (pH 8.4), all at a concentration of 1 mmol L^{-1}.

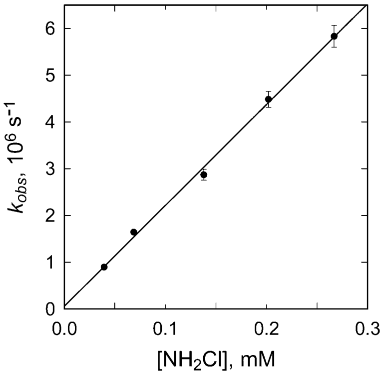

Figure 2. Rate constant for the decay of the e_{aq}^- absorption at 600 nm as a function of [NH$_2$Cl] in N$_2$-saturated solutions containing 0.1 mol L^{-1} of methanol at pH 9.9.

previously,[19] using a quartz cell with 2 cm optical path length. All experiments were carried out at room temperature, 22 ± 1 °C.

Results

The one-electron reduction and oxidation reactions of monochloramine in aqueous solutions were studied by radiolytic methods. The radiolysis of aqueous solutions leads to the production of various radicals and stable products.

$$H_2O \rightsquigarrow {}^{\bullet}OH, {}^{\bullet}H, e_{aq}^-, H^+, H_2O_2, H_2 \tag{6}$$

For γ or high-energy electron irradiation of dilute solutions, the primary radiation yields are the following: $G(e_{aq}^-) = 2.8$, $G({}^{\bullet}OH) = 2.8$, $G({}^{\bullet}H) = 0.6$, and $G(H_2O_2) = 0.75$, in units of 10^{-7} mol J^{-1}.

Reactions of Monochloramine with Primary Radicals of Water Radiolysis. To study the reactions of e_{aq}^- we used methanol as a scavenger for ${}^{\bullet}$OH and ${}^{\bullet}$H ($k_{OH} = 9.7 \times 10^8$ L mol^{-1} s^{-1}, $k_H = 2.6 \times 10^6$ L mol^{-1} s^{-1}).[20]

$$CH_3OH + {}^{\bullet}OH\ ({}^{\bullet}H) \rightarrow {}^{\bullet}CH_2OH + H_2O\ (H_2) \tag{7}$$

The rate constant for reaction of chloramine with e_{aq}^-,

$$NH_2Cl + e_{aq}^- \rightarrow {}^{\bullet}NH_2 + Cl^- \tag{8}$$

was determined by following the decay of the e_{aq}^- absorption at 600 nm as a function of [NH$_2$Cl] in N$_2$-saturated solutions containing 0.1 mol L^{-1} of methanol at pH 9.9 (Figure 2). The rate constant was found to be diffusion-controlled, $k_8 = (2.2 \pm 0.3) \times 10^{10}$ L mol^{-1} s^{-1}, where the indicated error limit includes both the statistical errors (±0.1) and the estimated uncertainty in the concentration (± 0.2). The concentration of ClO$^-$ in the solution was estimated to be <1% of [NH$_2$Cl] from the absorbance at 292 nm and thus cannot have any significant contribution to the measured rate constant. The value of k(NH$_2$Cl+e_{aq}^-) is identical with that reported previously[14] and comparable to k(O$_2$+e_{aq}^-) = 1.9×10^{10} L mol^{-1} s^{-1}, k(BrO$^-$+e_{aq}^-) = 1.5×10^{10} L mol^{-1} s^{-1}, and k(ClO$^-$+e_{aq}^-) = 7×10^9 L mol^{-1} s^{-1},[20] but much higher than k(NH$_2$OH+e_{aq}^-) = 9.2×10^8 L mol^{-1} s^{-1},[20] suggesting that chloramine is a much stronger oxidant than hydroxylamine.

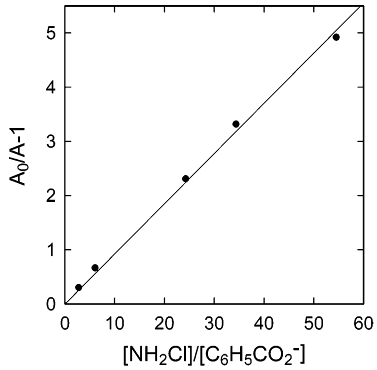

Figure 3. Rate constant for reaction of chloramine with hydroxyl radicals, determined by competition with the reaction of ${}^{\bullet}$OH with benzoate ions; the absorbance of the benzoate-OH adduct was monitored at 350 nm in N$_2$O-saturated solutions containing various concentrations of benzoate and chloramine at pH 9 with 2 mmol L^{-1} of borate.

To study the reactions of ${}^{\bullet}$OH radicals we saturated the solutions with N$_2$O to convert the e_{aq}^- into ${}^{\bullet}$OH ($k_9 = 9.1 \times 10^9$ L mol^{-1} s^{-1}).[20]

$$N_2O + e_{aq}^-\ (+H^+) \rightarrow N_2 + {}^{\bullet}OH \tag{9}$$

The rate constant for reaction of chloramine with ${}^{\bullet}$OH radicals was determined by competition kinetics, by using the reaction of ${}^{\bullet}$OH with benzoate ion as a reference reaction and monitoring the absorbance of the benzoate OH-adduct in the absence (A_0) and in the presence (A) of various concentrations of chloramine.

$$PhCO_2^- + {}^{\bullet}OH \rightarrow [HOPhCO_2^-]^{\bullet} \tag{10}$$

$$NH_2Cl + {}^{\bullet}OH \rightarrow {}^{\bullet}NHCl + H_2O \tag{11}$$

The adduct formed by reaction 10 was monitored at 350 nm.[21] At this wavelength [HOPhCO$_2^-$]$^{\bullet}$ has a molar absorption coefficient[22] of 3.6×10^3 L mol^{-1} cm^{-1} while the product of reaction 11, most likely ${}^{\bullet}$NHCl, has a relatively negligible absorbance (see below). The rate constant of reaction 10 was taken to be $k_{10} = (6.3 \pm 0.7) \times 10^9$ L mol^{-1} s^{-1}.[20,23] From the competition plot of ($A_0/A - 1$) vs the concentration ratio [NH$_2$Cl]/[PhCO$_2^-$] (Figure 3) we derive an apparent rate constant of $(5.8 \pm 0.64) \times 10^8$ L mol^{-1} s^{-1}. This value includes the contribution of reaction 11 as well as that of the reaction of residual NH$_3$ with ${}^{\bullet}$OH. Residual NH$_3$ exists, despite the high equilibrium constant of reaction 2, because excess NH$_4$Cl was used in the preparation of NH$_2$Cl to prevent the presence of the highly reactive ClO$^-$. At [NH$_2$Cl] = 2.8×10^{-3} mol L^{-1} we determined the ratio [NH$_2$Cl]/[NH$_3$] = 1.39 from the absorbance of NH$_2$Cl and the initial concentration of NH$_4$Cl used in the preparation. By taking k(${}^{\bullet}$OH+NH$_3$) = 9.9×10^7 L mol^{-1} s^{-1},[20] we derive $k_{11} = (5.1 \pm 0.6) \times 10^8$ L mol^{-1} s^{-1}. This value is lower than that derived[14] from competition with thiocyanate by a factor of 5. Although the thiocyanate competition method often

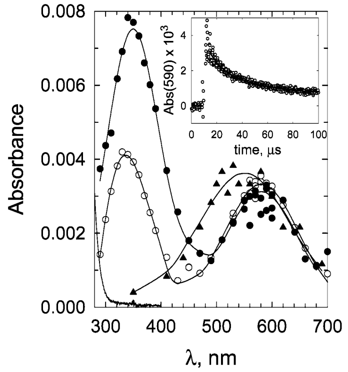

Figure 4. Transient absorption spectra of the $^•NH_2$, $^•NHCl$, and $NHClO_2^•$ radicals. The spectrum of $^•NH_2$ (▲) was monitored by pulse radiolysis of N_2O-saturated solution containing 0.1 mol L^{-1} of ammonia at pH 11. The other spectra were recorded with solutions of NH_2Cl (3.5 mmol L^{-1}) at pH 9 saturated with N_2O (○) or N_2O/O_2 (●). The former spectrum (○) is due mainly to the $^•NHCl$ radical, and its decay at 590 nm is shown in the insert. The latter spectrum (●) is due mainly to the $NHClO_2^•$ radical. The solid line spectrum between 280 and 400 nm shows the absorption of NH_2Cl at the same concentration as the radicals (23 μmol L^{-1}).

has provided reliable rate constants for hydroxyl radical reactions, it is likely that in the case of chloramine a thermal reaction with thiocyanate before the radiolysis may have led to erroneous results. Monochloramine is known to react with iodide, bromide, and cyanide ions[18,24,25] and is most likely to react with thiocyanate as well. The competition with benzoate does not suffer from such side reactions and we believe that the present result is more reliable. Our value of $k(^•OH+NH_2Cl)$ is higher than $k(^•OH+NH_3)$ by almost an order of magnitude but lower than $k(^•OH+NH_2OH)^{14,20} = 9 \times 10^9$ L mol^{-1} s^{-1} by more than an order of magnitude. The reactivity pattern toward $^•OH$ is similar to that observed for the substitution of Cl and OH on methane in the gas phase,[26] or on acetic acid in water,[20] and supports an abstraction mechanism.

The rate constant for reaction of monochloramine with hydrogen atoms was reported[14] to be $k(H^• + NH_2Cl) = (1.2 \pm 0.1) \times 10^9$ L mol^{-1} s^{-1} and was not determined in the present study. In principle, the reaction may take place via abstraction of hydrogen or chlorine. However, because of its high rate constant, by comparison to that of $^•OH$ radicals, the reaction was suggested[14] to involve chlorine abstraction.

$$NH_2Cl + H^• \rightarrow {}^•NH_2 + H^+ + Cl^- \tag{12}$$

Absorption Spectrum and Self-Reaction of the $^•NHCl$ Radical. The measurement of the absorption spectrum of $^•NHCl$ and the determination of the self-reaction kinetics are complicated by the relative slowness of the reaction of NH_2Cl with $^•OH$ and the rapidity of its reaction with e_{aq}^-. This leads to the need to correct for incomplete scavenging on one hand and for absorption due to $^•NH_2$ on the other. To do so, first, we redetermined the spectrum of $^•NH_2$ by pulse irradiating a N_2O-saturated solution containing 0.1 mol L^{-1} of ammonia at pH 11. The spectrum of the $^•NH_2$ radical was found to have only one peak at $\lambda_{max} = 530$ nm ($\epsilon_{530} = 80$ L mol^{-1} cm^{-1}) (Figure 4, solid triangles), in agreement with previous determinations.[27,28] Then we determined the spectrum of $^•NHCl$ from the pulse radiolysis of N_2O-saturated solutions containing $[NH_2Cl] = 3.5 \times 10^{-3}$ mol L^{-1} at pH 9. Two peaks were observed, at $\lambda_{max} = 330$ and 580 nm (Figure 4, open circles). We first correct the concentration of $^•NHCl$ for the incomplete scavenging of the $^•OH$ radicals and for the partial reaction of e_{aq}^- with NH_2Cl, and thus obtain preliminary molar absorption coefficients $\epsilon_{330} = (85 \pm 30)$ L mol^{-1} cm^{-1} and $\epsilon_{580} = (75 \pm 30)$ L mol^{-1} cm^{-1}. The value of ϵ_{580} was then corrected for the contribution of $^•NH_2$ (25−30%) to give $\epsilon_{580} = (56 \pm 30)$ L mol^{-1} cm^{-1}. Chlorine atom substitution thus leads to a 50-nm red shift in the maximum of the aminyl radical, indicating considerable interaction between the Cl atom and the unpaired electron.

Although the second peak of $^•NHCl$ is 10 nm lower than the peak of $CO_3^{•-}$, we have to consider whether part of this absorption may be due to $CO_3^{•-}$, since the molar absorption coefficient of $CO_3^{•-}$ at 600 nm is 30 to 40 times higher than that of $^•NHCl$.[29] The $CO_3^{•-}$ radicals may be formed by the reactions of $^•OH$ radicals with carbonate and bicarbonate that may be present as impurities ($k_{13} = 3.9 \times 10^8$ L mol^{-1} s^{-1}, $k_{14} = 8.5 \times 10^6$ L mol^{-1} s^{-1}).[20]

$$CO_3^{2-} + {}^•OH \rightarrow CO_3^{•-} \tag{13}$$

$$HCO_3^- + {}^•OH \rightarrow CO_3^{•-} \tag{14}$$

We remeasured the absorption due to $CO_3^{•-}$ in a N_2O-saturated solution of 0.1 mol L^{-1} of carbonate and obtained $\epsilon_{590} = (1930 \pm 110)$ L mol^{-1} cm^{-1}, in good agreement with the reported values of ϵ_{600}, in units of L mol^{-1} cm^{-1}, 1860,[30] 1910,[31] 1830,[32] 2200,[33] and 1500.[34] From our preparation method we estimate that the concentration of any carbonate impurity is <0.01 mmol L^{-1}. From the absorbance of the solution at 200 and 244 nm and the known spectra of chloramine[2,3,16] and carbonate (Figure 1) we can only estimate that the concentration of carbonate is <1 mmol L^{-1}. Increasing the pH from 9 to 10.9, to convert any residual bicarbonate ($pK_a(HCO_3^-) = 10.3$) into the more reactive carbonate, did not affect the transient absorbance at 590 nm. Moreover, addition of 1.5×10^{-3} mol L^{-1} of carbonate to the original solution at pH 9 also did not increase the absorbance at 590 nm. This amount is much more than the estimated upper limit of the impurity concentration. These experiments indicate that the peak at 580 nm can be ascribed to the $^•NHCl$ radical and that the contribution of carbonate is negligible.

The decay of $^•NHCl$ was monitored, in N_2O-saturated solutions containing two different concentrations of NH_2Cl, at 340 and 590 nm (Figure 4 insert) and the kinetic curves were fitted to a simple second-order rate law. With $[NH_2Cl] = 7.2 \times 10^{-3}$ mol L^{-1}, where most of the $^•OH$ radicals are scavenged by chloramines, but also ca. 40% of the e_{aq}^- are scavenged by chloramine in competition with N_2O, the observed rate constants at the two wavelengths were $2k_{340} = (4.1 \pm 1.0) \times 10^9$ L mol^{-1} s^{-1} and $2k_{590} = (2.6 \pm 1.0) \times 10^9$ L mol^{-1} s^{-1}, the uncertainty ranges primarily reflecting the uncertainties in the molar absorption coefficients. It should be pointed out, however, that these rate constants include contributions from other radical−radical reactions. By using $[NH_2Cl] = (3.6 \pm 0.2) \times 10^{-3}$ mol L^{-1}, where only ca. 25% of the e_{aq}^- are scavenged by chloramine, and monitoring the decay at 590 nm we found $2k = 2.8 \times 10^9$ L mol^{-1} s^{-1} at pH 9; 2.7×10^9 L mol^{-1} s^{-1} at pH 10.2; and 2.2×10^9 L mol^{-1} s^{-1} at pH 10.9, i.e., independent of pH within the above stated uncertainties. These measured values of $2k(^•NHCl)$ include a contribution from mixed decay with $^•NH_2$ radicals and are close to the value of $2k(^•NH_2) = (4.4 \pm 1) \times 10^9$ L mol^{-1} s^{-1}.[27,28]

The decay of the $^•NH_2$ radicals involves combination to form hydrazine.[28] Similarly, the decay of $^•NHCl$ radicals may proceed via combination to form initially the unstable dichlorohydrazine

(ClNHNHCl). This product may eliminate two molecules of HCl to leave N_2. Alternatively, it may eliminate only one molecule of HCl to leave the unstable HN═NCl, which may hydrolyze to form nitrosyl chloride (NOCl) and then nitrous acid (HNO_2) or nitrite ions. The latter products may be oxidized by the remaining NH_2Cl to form nitrate. In fact, reaction of aqueous ammonia with excess chlorine is known to produce N_2 along with smaller amounts of NO_2^- and NO_3^-.[35]

Reaction of Chloramine with $CO_3^{\bullet-}$ Radicals. To study the reaction of monochloramine with the carbonate radical we followed the decay of $CO_3^{\bullet-}$ in N_2O-saturated solutions with various NH_2Cl concentrations. With [carbonate] = 0.1 mol L^{-1} and $[NH_2Cl] = (1.5 \text{ to } 7.3) \times 10^{-4}$ mol L^{-1} at pH 10.24, most of the $^{\bullet}OH$ radicals react with carbonate. The decay of $CO_3^{\bullet-}$ took place in two steps (Figure 5a,b) and the rate of each step was dependent on the initial $[NH_2Cl]$. The decay curves could not be fitted to two consecutive irreversible first-order reactions involving an intermediate because the absorbance at the intermediate level as well as the decay in the slower step were dependent on $[NH_2Cl]$. Therefore, we assume that the absorbance at the end of the fast step is due mainly to $CO_3^{\bullet-}$ remaining in equilibrium and that the decay must involve more complex kinetics which can be fitted only by computer modeling. To model the observed kinetics in this complex system we took into account the reactions of $^{\bullet}OH$ radicals with carbonate (reaction 13, $k_{13} = 3.9 \times 10^8$ L mol^{-1} s^{-1})[20] and with chloramines (reaction 11, $k_{11} = 5.1 \times 10^8$ L mol^{-1} s^{-1}), the reactions of e_{aq}^- with N_2O (reaction 9, $k_9 = 9.1 \times 10^9$ L mol^{-1} s^{-1})[20] and with chloramine (reaction 8, $k_8 = 2.2 \times 10^{10}$ L mol^{-1} s^{-1}), and the reaction of $H^{\bullet}$ atoms with NH_2Cl (reaction 12, $k_{12} = 1.2 \times 10^9$ L mol^{-1} s^{-1}), neglecting the competing reaction of $H^{\bullet}$ with OH^- ($k = 2.5 \times 10^7$ L mol^{-1} s^{-1}). We also took into account the self-reaction of $^{\bullet}NH_2$ ($2k = 4.4 \times 10^9$ L mol^{-1} s^{-1}),[27] $^{\bullet}NHCl$ ($2k = 2.4 \times 10^9$ L mol^{-1} s^{-1}), and $CO_3^{\bullet-}$ ($2k$ determined to be 1.1×10^7 L mol^{-1} s^{-1}, in agreement with previous values[36]), and an estimated value for the radical−radical reaction $CO_3^{\bullet-} + {}^{\bullet}NH_2$ ($k = 1.5 \times 10^9$ L mol^{-1} s^{-1}). The observed kinetics were best fit by assuming an equilibrium reaction 15,

$$CO_3^{\bullet-} + NH_2Cl \leftrightarrows [CO_3NH_2Cl]^{\bullet-} \qquad (15)$$

with $k_{15} = 2.5 \times 10^5$ L mol^{-1} s^{-1} and $k_{-15} = 4 \times 10^2$ s^{-1} ($K_{15} = 625$ L mol^{-1} and $\Delta G_{15} = -16.5$ kJ mol^{-1}), and decomposition of the complex with $k_{16} = 7 \times 10^2$ s^{-1}.

$$[CO_3NH_2Cl]^{\bullet-} \rightarrow HCO_3^- + {}^{\bullet}NHCl \qquad (16)$$

We estimate that the uncertainties in the rate and equilibrium constants for these reactions from this model study are better than a factor of 2. The observed kinetics and the above model also permit us to estimate an upper limit for the rate constant of reaction 17.

$${}^{\bullet}NH_2 + HCO_3^- \rightarrow NH_3 + CO_3^{\bullet-} \qquad (17)$$

By assuming that <10% of the $^{\bullet}NH_2$ radicals react with carbonate (to fit the model), we estimate $k_{17} < 5 \times 10^3$ L mol^{-1} s^{-1}, close to an earlier estimate.[37]

At a lower concentration of carbonate (0.01 mol L^{-1}), the $^{\bullet}OH$ radicals react with both carbonate and chloramine and then the contribution of the cross-reaction $CO_3^{\bullet-} + {}^{\bullet}NHCl$ becomes important. A rate constant of 6×10^8 L mol^{-1} s^{-1} was derived from the modeling to fit the kinetic traces (Figure 5c) and is estimated to have an uncertainty of about a factor of 2. This value is about half the rate constant estimated above for the cross reaction between $CO_3^{\bullet-}$ and $^{\bullet}NH_2$ radicals.

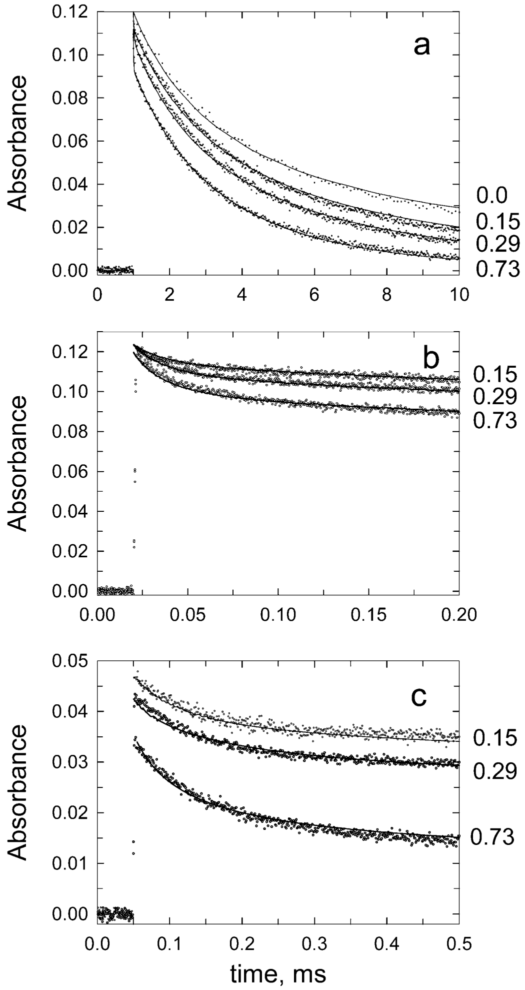

Figure 5. Kinetic traces showing the decay of the carbonate radical absorption at 600 nm in the presence of chloramine at pH 10.2: (a and b) 0.1 mol L^{-1} of carbonate and (c) 0.01 mol L^{-1} of carbonate. The concentration of NH_2Cl, in mmol L^{-1}, is indicated on the right of each trace; the radical concentration was 1.6×10^{-6} mol L^{-1}.

Reaction of $^{\bullet}NHCl$ with O_2. To study the reaction of $^{\bullet}NHCl$ radicals with O_2, we carried out pulse radiolysis experiments with NH_2Cl solutions saturated with a mixture of N_2O and O_2. The spectrum of the expected peroxyl radical, $NHClO_2^{\bullet}$, was measured with different concentrations of O_2. Two peaks were observed, at 350 and 580 nm (Figure 4, solid circles). By correcting the concentration of $^{\bullet}NHCl$ for the partial scavenging of the $^{\bullet}OH$ radicals by NH_3 and for the partial reaction of e_{aq}^- with NH_2Cl (see above), and assuming that all $^{\bullet}NHCl$ radicals reacted with O_2 (at $[O_2] = 4.8 \times 10^{-4}$ mol L^{-1}), we determined a molar absorption coefficient of $\epsilon_{350} = (190 \pm 30)$ L mol^{-1} cm^{-1}. It was noticed, however, that increasing the concentration of O_2 leads to an increase in the absorbance at 350 nm and a decrease at 580 nm. This may be interpreted as an increase in $[NHClO_2^{\bullet}]$ accompanied by a decrease in $[{}^{\bullet}NHCl]$ as a result of a fast equilibrium reaction.

$$NHClO_2^{\bullet} \leftrightarrows {}^{\bullet}NHCl + O_2 \qquad (18)$$

The alternative explanation of competition between the formation of $NHClO_2^{\bullet}$ and its subsequent fast decay by reaction with $^{\bullet}NHCl$ is ruled out by the fact that the rate of decay at 350 nm did not increase with the concentration of O_2. Formation of

TABLE 1: Comparison of Experimental and Calculated Absorbance at 350 nm

$[O_2]$ (10^{-4} mol L^{-1})	A_{exp}	A_{calc}
0	0.0043	0.0043
1.5	0.0057	0.0052
2.2	0.0063	0.0062
2.6	0.0064	0.0064
2.7	0.0065	0.0064
2.9	0.0062	0.0065
3.1	0.0063	0.0065
4.3	0.0071	0.0072
5.5	0.0081	0.0079

$NH_2O_2^\bullet$ should not be important in this system because the rate constant for the reaction of $^\bullet NH_2$ with O_2 ($k_{-18} = 3 \times 10^8$ L mol^{-1} s^{-1}) is slower than that observed in our experiments.

From the dependence of the absorbance at 350 nm upon $[O_2]$ in a N_2O/O_2 saturated solution of chloramine (3.5×10^{-3} mol L^{-1}), by fitting the measured absorbance (A) with the equation $A/(l[R]) = \{\epsilon_{350}(^\bullet NHCl) + \epsilon_{350}(NHClO_2^\bullet)K_{18}[O_2]\}/(1 + K_{18}[O_2])$, where l is the optical path length and [R] is the initial concentration of $^\bullet$NHCl (26.9 μmol L^{-1}), we derive an equilibrium constant $K_{18} = (3 \pm 2) \times 10^{-3}$ mol L^{-1} ($\Delta G_{18} = 14.5$ kJ mol^{-1}) and a molar absorption coefficient $\epsilon_{350}(NHClO_2^\bullet) = (1000 \pm 600)$ L mol^{-1} cm^{-1}. Table 1 shows the agreement between the experimentally determined absorbance and that calculated from the above parameters at different O_2 concentrations. From K_{18} we estimate that at $[O_2] = 5 \times 10^{-4}$ mol L^{-1} only 17% of the radicals are present as $NHClO_2^\bullet$, and if we assume that this radical does not absorb at 580 nm, we expect the absorbance at this wavelength to decrease by 17% in the presence of this concentration of O_2. The decrease, in fact, was by about 10%, in reasonable agreement within the estimated uncertainties. The spectrum of $NHClO_2^\bullet$, with $\lambda_{max} = 350$ nm, is close to that reported for $NH_2O_2^\bullet$ ($\lambda_{max} = 340$ nm). The decay of the absorbance at 350 nm is due to the self-decay of $NHClO_2^\bullet$ and of $^\bullet$NHCl and their cross reaction and the kinetic curves were too noisy to permit clear distinction between first-order and second-order rate laws. The self-decay of $NHClO_2^\bullet$ may produce O_2 and unstable products such as ClHNOONHCl or the radical $NHClO^\bullet$ and subsequent reactions may lead to formation of stable products such as nitrite or nitrate.

Discussion

The rate constant for the reaction of NH_2Cl with e_{aq}^- is comparable to the rate constants[20] for reactions of O_2 and BrO^- but much higher than that of NH_2OH, indicating that monochloramine is a much stronger oxidant than hydroxylamine. The one-electron reduction potential of monochloramine $E(NH_2Cl/^\bullet NH_2,Cl^-)$ can be estimated from $\Delta_f G(Cl^-)$ (-131.2 kJ mol^{-1}),[38] $\Delta_f G(^\bullet NH_2)$ (192 kJ mol^{-1}),[13] and $\Delta_f G(NH_2Cl)$ (70.3 kJ mol^{-1}) (this latter value is derived from the most recent publication[5] and a measure of its uncertainty is reflected in the earlier reported values: 84,[17] 77.4,[39] and 66.9[3] kJ mol^{-1}). From these values we calculate $E(NH_2Cl/^\bullet NH_2,Cl^-) = 0.1$ V. This potential is close to $E(HOBr/HOBr^{\ -}) = 0.14$ V and higher than $E(H_2O_2/OH,OH^-) = -0.03$ V, $E(HO_2^-/O^-,OH^-) = -0.04$ V, $E(O_2/O_2^-) = -0.16$ V, and $E(BrO^-/Br^-,O^-) = -0.24$ V; all of these oxidants react with hydrated electrons with practically diffusion-controlled rate constants. Hydroxylamine reacts more slowly with e_{aq}^- because $E°(NH_2OH/NH_2^\bullet,OH^-)$ is more negative than these values. Although $E°(NH_2OH/NH_2^\bullet,OH^-)$ was estimated to be -0.12 V,[13] the value of $\Delta_f G(NH_2OH(aq))$ used in that estimation has been corrected,[40] and this correction leads to $E°(NH_2OH/NH_2^\bullet,OH^-) \approx -0.6$ V (based on the value $\Delta_f G°$(aq NH_2)[13] = 192 kJ mol^{-1}, $\Delta_f G°$(aq OH^-)[38] = -157.3 kJ mol^{-1}, and $\Delta_f G°$(aq NH_2OH)[41] = -23.4 kJ mol^{-1}). Thus the reduction potential of chloramine is more positive than that of hydroxylamine by about 0.7 V, in line with the much higher rate constant for reaction of chloramine with e_{aq}^-.

TABLE 2: Calculated N−H Bond Dissociation Energies and Rate Constants for $^\bullet$OH Reactions

compd (S)	UHF/6-31G* (kJ mol^{-1})	CBS-Q (kJ mol^{-1})	$k_{(OH+S)}$ (L mol^{-1} s^{-1})
NH_3	337	444.5	8.2×10^7
NH_2Cl	298	379.8	5.2×10^8
NH_2OH	265	349	9.5×10^9

The rate constant for the reaction of NH_2Cl with $^\bullet$OH radicals is higher than that of NH_3 by almost an order of magnitude and lower than that of NH_2OH by more than an order of magnitude, which suggests a hydrogen abstraction mechanism. The N−H bond dissociation energy of NH_3 is[42] 455 kJ mol^{-1} but the values for NH_2OH and NH_2Cl are not known. Therefore, we computed all three values in the gas phase by using Gaussian 98[43] with two approximation methods (Table 2). Although the CBS-Q method gives a value for NH_3 that is very close to the experimentally determined value, both methods show that the N−H bond dissociation energy increases in the order NH_2OH, NH_2Cl, NH_3. The measured rate constants decrease in that order, in line with an H-abstraction mechanism.

From the N−H bond dissociation energies calculated by the CBS-Q method (Table 2), if we assume that the differences between the respective enthalpies are the same in water as in the gas phase and that the entropies of dissociation of these bonds in NH_3, NH_2Cl, and NH_2OH are similar, we can estimate the differences between the potentials $E(NH_3^{\bullet +}/NH_3)$, $E(^\bullet NH_2Cl^+/NH_2Cl)$, and $E(^\bullet NH_2OH^+/NH_2OH)$. The reduction potential $E(NH_3^{\bullet\ +}/NH_3) = 2.13$ V was calculated by Stanbury,[13] who chose $pK_a(NH_3^{\bullet +}) = 2.3$. From this value and the above assumptions we estimate for chloramine $E(^\bullet NHCl,H^+/NH_2Cl) = 1.7$ V ($pK_a(NH_2Cl^{\bullet +})$ is unknown) and for hydroxylamine $E(^\bullet NH_2OH^+/NH_2OH) = 1.03$ V or $E(^\bullet NHOH,H^+/NH_2OH) = 1.28$ V (by using $pK_a(NH_2OH^{\bullet +}) = 4.2$). A slightly lower reduction potential, $E(^\bullet NH_2OH^+/NH_2OH) = 0.91$ V, was estimated before,[40] by using ab initio calculation of $\Delta_f H(NH_2O)$, semiempirical (AM1) calculation of $S(NH_2O)$, and assuming that the free energy of hydration of NH_2O and NH_3 are the same (-10 kJ mol^{-1}). From the two values we suggest that $E(^\bullet NH_2OH^+/NH_2OH)$ lies between 0.9 and 1.1 V.

In summary, chloramine reacts very rapidly with solvated electrons to form $^\bullet NH_2$ and somewhat more slowly with the hydroxyl radical to form $^\bullet$NHCl. Chloramine reacts with the carbonate radical to form an intermediate complex and then $^\bullet$NHCl. On the basis of the results with carbonate it is expected that other strong oxidants also will react with chloramine to produce $^\bullet$NHCl. Both $^\bullet NH_2$ and $^\bullet$NHCl radicals decay via radical−radical reactions and can react with O_2 to form peroxyl radicals. The $NH_2O_2^\bullet$ radical has been shown before to eliminate water and produce NO.[27] The fate of the $NHClO_2^\bullet$ radical is unclear because it is present in a mixture with $^\bullet$NHCl and the decay involves various reactions.

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