The Rate and Equilibrium Constants for the Reaction $NO_3^\bullet + Cl^- \rightleftarrows NO_3^- + Cl^\bullet$ in Aqueous Solutions

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The rate and equilibrium constants for the reaction $NO_3^\bullet + Cl^- \rightleftarrows NO_3^- + Cl^\bullet$ in aqueous solutions were measured by pulse radiolysis. The formation and decay of the nitrate radical, $NO_3^\bullet$, and the dichloride radical anion, $Cl_2^{\bullet-}$, in irradiated aqueous solutions containing nitric acid and chloride ions were followed under various conditions. Because of the complexity of the system, the forward rate constant and the equilibrium constant were derived from modeling the experimental results, including secondary formation and decay reactions. The modeling study results in an equilibrium constant of $K_{eq} = (3.5 \pm 0.5)$ at an ionic strength between 0.1 and 1 mol L^{-1} and a forward rate constant $k_1 = (3.5 \pm 0.5) \times 10^8$ L mol^{-1} s^{-1}. In contrast with previous reports, no effect of ionic strength (up to 2 mol L^{-1}) on the forward rate constant was observed.

Introduction

The nitrate radical, $NO_3^\bullet$, is the most important radical in the atmosphere at night. It is formed by the reaction of nitrogen dioxide with ozone and exists in equilibrium with dinitrogen pentoxide.[1] The $NO_3^\bullet$ radical is a very strong oxidant; thus, the chemistry of $NO_3^\bullet$ in the aqueous phase of the atmosphere may involve reactions with water as well as reactions with the other constituents of the solution, such as Cl^-, HSO_3^-, Fe^{II}, or Mn^{II}. Because of the relatively high chloride ion concentration in marine clouds and aerosols, the reaction

$$NO_3^\bullet + Cl^- \rightleftarrows NO_3^- + Cl^\bullet \tag{1}$$

that leads to formation of the less reactive radical, $Cl_2^{\bullet-}$,

$$Cl^\bullet + Cl^- \rightleftarrows Cl_2^{\bullet-} \tag{2}$$

and then to molecular chlorine,

$$2Cl_2^{\bullet-} \rightarrow Cl_2 + 2Cl^- \tag{3}$$

is of particular interest.

There have been several determinations of the rate constant for the forward reaction 1 at room temperature.[2−5] The rate constant values reported for this important reaction vary by a factor of 36. It was suggested that this variation is due to a strong ionic strength dependence for the reaction.[4,6] More recent work indicated that the ionic strength dependence is less important, but still significant.[5] In that work, the rate constant for the reverse reaction −1 was determined by generating chlorine atoms through the flash photolysis of chloroacetone in the presence of nitrate. A rate constant of $k_{-1} = (1.02 \pm 0.04) \times 10^8$ L mol^{-1} s^{-1} was reported.

The experimental indication that the kinetics of reactions involving the neutral radical $NO_3^\bullet$ is significantly affected by ionic strength, even for reactions with neutral molecules,[6] is of great importance to chemical kinetics. Although the role of ionic strength in reactions of neutral species has been known for some time,[7] the magnitude of the effect has generally been thought to be far less than the effect of ionic strength on reactions of ions. Essentially, this effect arises from the second term in the expanded Debye−Hückel relationship for the activity coefficient, which leads to the following expression for the rate constant at any ionic strength:

$$\log k = \log k_o - \frac{-z_a z_b A\sqrt{\mu}}{1 + Ba\sqrt{\mu}} + C\mu \tag{4}$$

where k_o is the rate constant at zero ionic strength, μ is the ionic strength, A and B are collections of physical constants, a is the distance of closest approach, and C is an unknown constant. The other two parameters, z_a and z_b, are the charges on the reactants thus, when z_a or $z_b = 0$:

$$\log k = \log k_o + C\mu \tag{5}$$

and the logarithm of the rate constant is expected to show a linear dependence on the ionic strength.

Although the parameters A and B can be calculated, and a estimated, there is no reliable method of calculating C, which must be determined by experiment. Kinetic studies on many different ion−ion reactions have demonstrated that for low to moderate ionic strengths, $\mu < 0.1$ mol L^{-1}, the rate constant is proportional to $\sqrt{\mu}$, indicating that $A \gg C$.[8] Indeed, a study of the influence of ionic strength on the reaction

$$SO_4^{\bullet-} + Cl^- \rightarrow SO_4^{2-} + Cl^\bullet \tag{6}$$

showed a very good fit with $C = 0$ up to $\mu = 0.4$ mol L^{-1}.[9] Thus, it was surprising to see that the reaction of $NO_3^\bullet$ with

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Cl^- showed an ionic strength effect about half that determined for the reaction of $SO_4^{\bullet -}$ with Cl^- up to $\mu = 0.4$ mol L^{-1}.[6]

The present study was also prompted by our recent results on the reaction of ${}^\bullet OH$ radicals with nitric acid,[10]

$$^\bullet OH + HNO_3 \rightleftarrows H_2O + NO_3^\bullet \qquad (7)$$

which lead to a value of $K_5 = (2.8 \pm 0.4) \times 10^5$ extrapolated to zero ionic strength. This equilibrium constant leads to a reduction potential of $E°(NO_3^\bullet/NO_3^-) = (2.58 \pm 0.02)$ V (see below). But the recent results of Buxton et al.[5] on the reaction of $NO_3^\bullet$ with Cl^- suggest a potential about 0.1 V lower.

Because of the great importance of reaction 1 in atmospheric droplets and the considerable impact of a nonnegligible effect of ionic strength on reactions of neutral radicals, we have undertaken a re-determination of the rate constant of this reaction by pulse radiolysis. In the present study, we derive the forward rate constant by kinetic techniques and also derive the equilibrium constant from the transient absorbance of the radicals. Computer modeling is utilized to analyze the experimental results in order to take into account secondary radical reactions.

Experimental Section[11]

The $NO_3^\bullet$ radicals and $Cl^\bullet$ atoms were generated by reaction of nitric acid and chloride ions with ${}^\bullet OH$ radicals in irradiated aqueous solutions. The formation and decay of the absorbing species were followed by kinetic spectrophotometric pulse radiolysis.

Fresh solutions were prepared with analytical grade HNO_3 (Fluka), $NaNO_3$ (Alfa), and NaCl (Mallinckrodt); $HClO_4$ (Mallinckrodt) was used to increase the acidity and $NaClO_4$ (Fluka) to increase the ionic strength. Water was purified with a Millipore Super-Q system. The solutions were deoxygenated by bubbling with ultrahigh purity nitrogen. Electron pulses from a Varian linear accelerator, with a pulse duration generally between 0.1 and 1 μs, provided doses in the range of 3 to 30 Gy, producing ${}^\bullet OH$ radicals at concentrations of 2 to 18 μmol L^{-1}. The irradiation zone was masked to 1 cm, significantly smaller than the radiation beam width, to achieve uniform radical concentration throughout the monitored solution volume. The total concentration of radicals ($[{}^\bullet OH]_o = [{}^\bullet OH] + [NO_3^\bullet]$) formed in nitric acid solutions ($0.1 \leq [NO_3^-] \leq 1$ mol L^{-1}) was determined by adding 1 mmol L^{-1} SCN^- and measuring the yield of $(SCN)_2^{\bullet -}$, taking a molar absorption coefficient $\epsilon((SCN)_2^{\bullet -}) = 7580$ L mol^{-1} cm^{-1} at $\lambda = 472$ nm.[12] The $NO_3^\bullet$ radical was monitored at 641 nm and the $Cl_2^{\bullet -}$ radical was monitored at 340 nm (see below). The kinetics of $NO_3^\bullet$ and $Cl_2^{\bullet -}$ formation and decay were investigated at different concentrations of chloride (from 5×10^{-5} to 4×10^{-3} mol L^{-1}) and nitric acid (from 0.1 to 1.0 mol L^{-1}). All experiments were carried out at room temperature, (20 ± 2) °C.

Results

The following primary species are produced in irradiated water:

$$H_2O \rightsquigarrow {}^\bullet OH, {}^\bullet H, e_{aq}^-, H^+, H_2O_2, H_2 \qquad (8)$$

For high-energy electron irradiation of dilute solutions, the primary radiation yields are: $G(e_{aq}^-) = 0.28$ μmol J^{-1}, $G({}^\bullet OH) = 0.28$ μmol J^{-1}, $G({}^\bullet H) = 0.06$ μmol J^{-1}, and $G(H_2O_2) = 0.075$ μmol J^{-1}.[13] In N_2-saturated solutions containing nitric acid and chloride ions, the hydroxyl radicals react with HNO_3 or with Cl^-,

$$^\bullet OH + HNO_3 \rightleftarrows H_2O + NO_3^\bullet \qquad (7)$$

$$^\bullet OH + Cl^- \rightleftarrows {}^\bullet ClOH^- \; (+ H^+ \rightarrow Cl^\bullet + H_2O) \qquad (9)$$

the solvated electrons react very rapidly with NO_3^- and with H^+,

$$e_{aq}^- + NO_3^- \rightarrow NO_3^{\bullet 2-} \; (+ H^+ \rightarrow NO_2^\bullet + OH^-) \qquad (10)$$

$$e_{aq}^- + H^+ \rightarrow {}^\bullet H \qquad (11)$$

and the ${}^\bullet H$ atoms react with NO_3^-:

$$^\bullet H + NO_3^- + H^+ \rightarrow NO_2^\bullet + H_2O \qquad (12)$$

Thus several radicals are produced in this system, which engage in various subsequent reactions, leading to a complex chemical system. Because of this complexity, an accurate value of the equilibrium constant for reaction 1 cannot be determined simply from the absorbance at equilibrium or from the kinetics of approach to equilibrium. Similarly, accurate kinetics cannot be determined simply from the rates of decay or formation of $NO_3^\bullet$ and $Cl_2^{\bullet -}$ radicals because of the contributions of competing reactions. Computer modeling is necessary to take into account all of these competing reactions.

The Molar Absorption Coefficient of the Dichloride Radical Anion. The determination of the kinetics for reaction 1 by modeling requires that we know the absolute concentrations of both $NO_3^\bullet$ and $Cl_2^{\bullet -}$. We use the molar absorption coefficient of the $NO_3^\bullet$ radical determined in this laboratory,[10] $\epsilon(NO_3^\bullet)_{641} = (1130 \pm 50)$ L mol^{-1} cm^{-1} and $\epsilon(NO_3^\bullet)_{340} \approx 390$ L mol^{-1} cm^{-1}. We have re-determined the value for $Cl_2^{\bullet -}$. This latter value was measured at 340 and 350 nm by pulse irradiating aqueous solutions at pH 1 which contained either NaCl (2.5×10^{-2} mol L^{-1}) or KSCN (1×10^{-2} mol L^{-1}). The pH was adjusted with $HClO_4$ in both cases and the solutions were pulse irradiated both under air and after purging with nitrogen. By assuming that the yield of $Cl_2^{\bullet -}$ is equal to the yield of $(SCN)_2^{\bullet -}$, we determined $\epsilon(Cl_2^{\bullet -})_{340} = (8800 \pm 650)$ L mol^{-1} cm^{-1} and $\epsilon(Cl_2^{\bullet -})_{350} = (8450 \pm 630)$ L mol^{-1} cm^{-1}. Our value is identical with that reported by Jayson et al.[14] at 340 nm and we agree very closely with the value of 8600 L mol^{-1} cm^{-1} at 345 nm reported by Kim and Hamill.[2] Our result is somewhat higher than the value of Lierse et al.[15] of 8100 L mol^{-1} cm^{-1} and lower than the value of Adams et al.[16] of 9600 L mol^{-1} cm^{-1}, both at 340 nm. In addition, we determined $\epsilon(Cl_2^{\bullet -})_{641} \leq 90$ L mol^{-1} cm^{-1}.

Experimental Results on Equilibrium 1. The following experimental results point to the existence of equilibrium 1. Figure 1 shows representative kinetic traces at various concentrations of HNO_3 and Cl^- monitored by absorbance at 641 nm and at 340 nm. These follow the formation and decay of the $NO_3^\bullet$ and $Cl_2^{\bullet -}$ radicals, respectively. In all cases, the absorbance at these wavelengths increases to a maximum and then decreases to zero. For the discussion below, we define A_{max} as the maximum absorbance in the kinetic trace, corresponding to a maximum in the concentration of the radical being monitored. The time at which A_{max} is reached is different for the two wavelengths, indicating that the two reactants are not merely competing for the primary oxidizing radicals but rather that the chlorine species is formed at least in part by reaction 1. From these and other traces we find that A_{max} at 641 nm increases

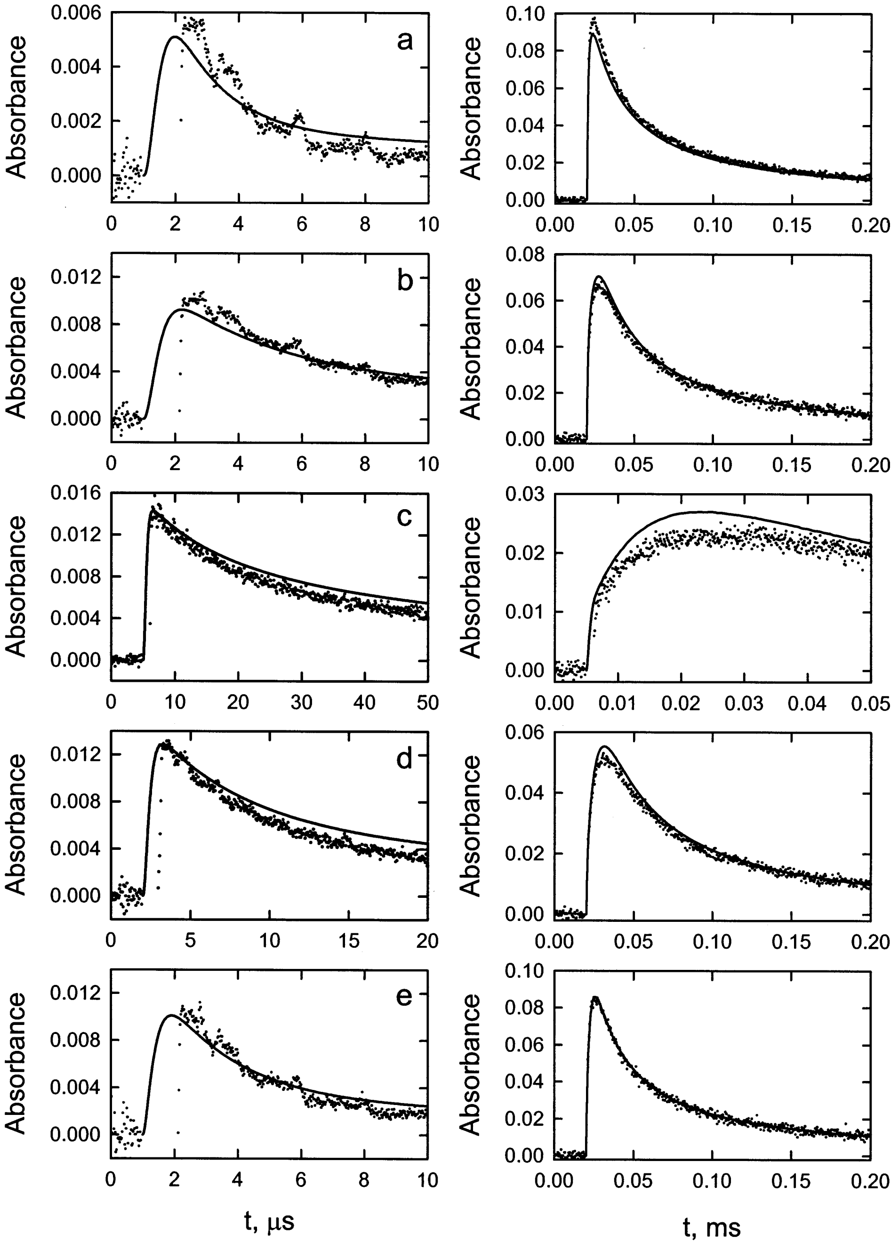

Figure 1. Kinetic traces for the formation and decay of the $NO_3^•$ radical, monitored at 641 nm (left), and the $Cl_2^{•-}$ radical, monitored at 340 nm (right), following pulse irradiation of deoxygenated aqueous solutions containing various concentrations of nitric acid and chloride ions: (a) 0.2 mol L^{-1} HNO_3, 3 mmol L^{-1} Cl^-; (b) 0.4 mol L^{-1} HNO_3, 2 mmol L^{-1} Cl^-; (c) 1.0 mol L^{-1} HNO_3, 1 mmol L^{-1} Cl^-; (d) 1.0 mol L^{-1} HNO_3, 2 mmol L^{-1} Cl^-; (e) 1.0 mol L^{-1} HNO_3, 4 mmol L^{-1} Cl^-. The curves were calculated by modeling the reactions given in Table 1 (see text for details).

with an increase in [HNO_3] but decreases with an increase in [Cl^-] (Figure 2). Inversely, A_{max} at 340 nm increases with [Cl^-] but decreases with an increase in [HNO_3] (Figure 3). These results point to the existence of an equilibrium reaction, although due to loss processes, the values of A_{max} do not represent this equilibrium alone.

An increase in the concentration of Cl^- leads to a more rapid and more complete reaction of $NO_3^•$ radicals with Cl^- to form $Cl_2^{•-}$, until the concentration of the latter species approaches the initial concentration of the hydroxyl radicals, [$^•OH$]$_o$. Under these conditions, the decay of $Cl_2^{•-}$ follows a second-order rate law and the rate constant was calculated to be $k_3 = (2.0 \pm 0.3) \times 10^9$ L mol^{-1} s^{-1}, in line with most of the values reported in the literature.[17]

The observed formation of the absorption at 340 nm does not follow a simple first-order rate law because of the various radical−radical reactions that take place concurrently with reaction 1. As the first step in the evaluation of the results, we approximated the experimental traces to a first-order rate (k_{obs}). The value of k_{obs} increases with [Cl^-] but decreases with [HNO_3] (Figure 4). The latter observation is due to the fact that when the concentration of nitric acid is increased, the contribution of the rapid reaction 9 is diminished compared with that of reaction 7 and the formation of $Cl^•$ is now due more to the slower reaction 1. The dependences of k_{obs} and A_{max} on [Cl^-] in Figures 2−4 were obtained both at pH 0 (1 mol L^{-1} HNO_3) and at pH 0.7 (0.2 mol L^{-1} HNO_3).

Modeling Studies. To derive more accurate values for rate and equilibrium constants for reaction 1, we modeled the kinetics of formation and decay of $NO_3^•$ and $Cl_2^{•-}$. The modeling was carried out with the kinetic scheme summarized in Table 1. The scheme includes the equilibrium reactions 1, 7, and 13; the reactions of the primary radicals with the various solutes and subsequent equilibria of the species produced, and finally, the

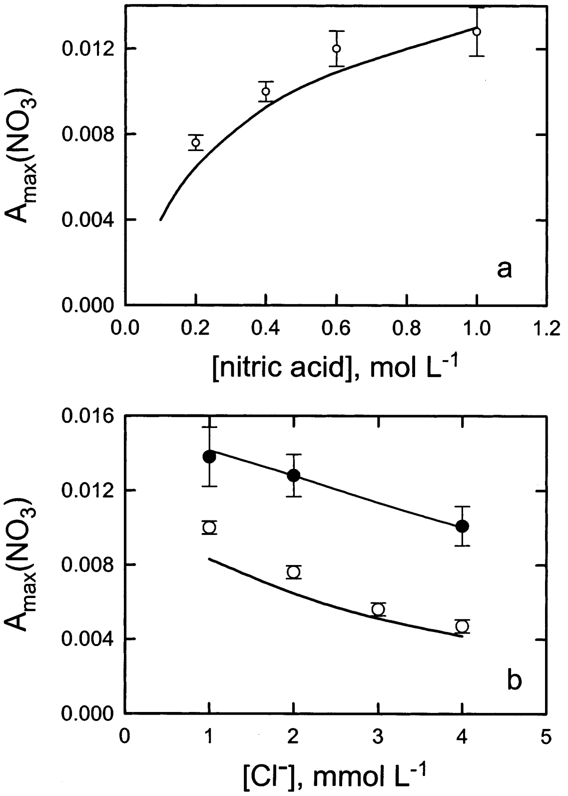

Figure 2. The maximum absorbance at 641 nm (nitrate radicals) produced by a 23 Gy electron pulse (a) as a function of nitric acid concentration ($[Cl^-] = 2$ mmol L^{-1}), and (b) as a function of chloride concentration ($[HNO_3] = 0.2$ mol L^{-1} (○) and 1 mol L^{-1} (●)).

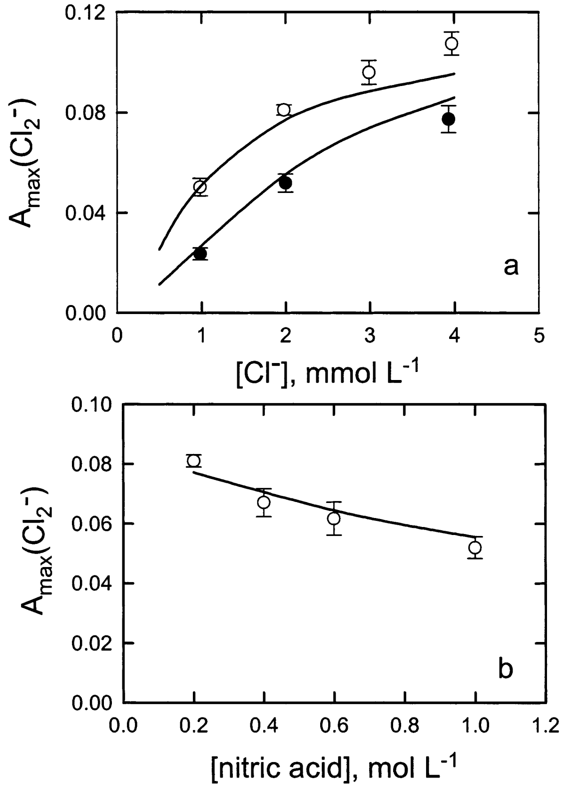

Figure 3. The maximum absorbance at 340 nm ($Cl_2^{\bullet-}$ radicals) produced by a 23 Gy electron pulse (a) as a function of chloride concentration ($[HNO_3] = 0.2$ mol L^{-1} (○) and 1 mol L^{-1} (●)), and (b) as a function of nitrate concentration ($[Cl^-] = 2$ mmol L^{-1}).

various radical−radical reactions expected in the system (reactions 3 and 16−31). Except for the rate constant for the forward reaction of $NO_3^{\bullet}$ with Cl^- (reaction 1) the rate constants were taken from the literature where possible, including the value of k_{-1}, which was taken from the recent paper by Buxton et al.,[5] where it was measured directly by flash photolysis in the absence of Cl^- ions. In addition to the known reaction of $H^{\bullet}$ with NO_3^-, we considered the reaction of $H^{\bullet}$ with HNO_3, which has not been reported. If this reaction proceeds to form $NO_2^{\bullet}$, it has no effect. But if the reaction proceeds by abstraction to form $NO_3^{\bullet}$ (reaction 14), it has a significant impact on the model output if $k_{14} > 1 \times 10^7$ L mol^{-1} s^{-1}. This value is significantly greater than the upper limit reported for this reaction in the gas phase.[18] The value of k_3 was determined in the present study and is identical to values reported in several earlier studies.[17] Reaction 30 was introduced in order to account for the expected radical−radical reaction when both $NO_3^{\bullet}$ and $Cl_2^{\bullet-}$ are present. This reaction appears to be important in this system and although its rate constant is not known, it must be within an order of magnitude of the diffusion-controlled limit. This is expected for an electron-transfer reaction with a very high driving force ($E(Cl_2/Cl_2^{\bullet-}) = 0.70$ V[19] and $E°(NO_3^{\bullet}/NO_3^-) = 2.48$ V, see below). The value of k_{30} that gives the best fit to the present results is 1×10^9 L mol^{-1} s^{-1}. If we choose a lower value, reaction 30 will have a minimal effect on the decay kinetics; if we choose a higher value, the calculated decay will appear to be much faster than the experimentally observed decay. In parallel with reaction 30, we introduced reaction 31 and initially assumed a similar rate constant. Reactions 30 and 31 have the same effect on the decay kinetics of $Cl_2^{\bullet-}$ radicals but opposite effects on the decay kinetics of $NO_3^{\bullet}$ radicals. From the modeling we determined that this value is an upper limit for k_{31}. Of the other radical−radical reactions in Table 1, the reactions of the hydroxyl radical have little effect on the model results, due, primarily, to the dominance of reactions 7 and 9. On the other hand, reactions of hydrogen atoms with other radicals have an observable effect, since the main reaction of hydrogen atoms with a molecule is reaction 12, which is slow. Reaction of $Cl_2^{\bullet-}$ with nitrate ions was found to have no observable effect on the modeling results.

The radical formation rate during the pulse is essentially linear. For modeling purposes, we combined two exponential formation rates with rate constants such that the formation of the radicals was 90% complete within the pulse width of ≈ 1 μs.

Figures 1−4 show the experimental results along with the curves calculated from the model (taking into account the absorbance of $NO_3^{\bullet}$ and $Cl_2^{\bullet-}$ both at 340 and 641 nm). The best fit was obtained with the value of $k_1 = (3.5 \pm 0.5) \times 10^8$ L mol^{-1} s^{-1}. In addition, we carried out calculations setting the rate constant for reaction −7 to zero. No effect on the calculated curves was found, showing that this reaction becomes unimportant when $[Cl^-] \geq 1 \times 10^{-3}$ mol L^{-1}, as expected on the basis of the rate constants in Table 1.

The effect of a change in ionic strength on this reaction system was investigated by using 0.2 mol L^{-1} HNO_3 solutions containing Cl^- at concentrations between 5×10^{-5} and 4×10^{-3} mol L^{-1} and adding up to 2 mol L^{-1} $NaClO_4$. The kinetic traces were fitted to a first-order rate equation to obtain k'_{obs}. Figure 5a shows the dependence of k'_{obs} on $[Cl^-]$ and Figures 5b and 5c show typical traces in the absence and presence of 2 mol L^{-1} $NaClO_4$. Within the experimental uncertainty, no effect of the ionic strength on the kinetics of decay of $NO_3^{\bullet}$ was observed.

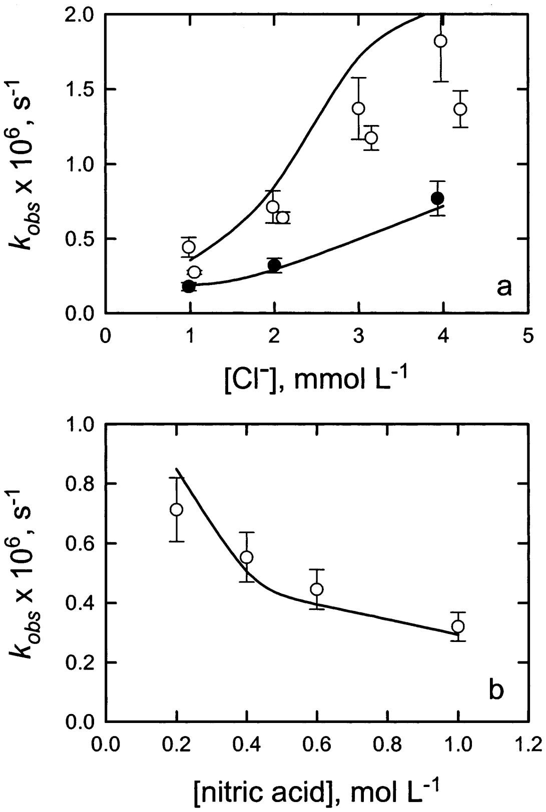

Figure 4. The observed rate of formation of the absorbance at 340 nm ($Cl_2^{\bullet-}$ radicals) (a) as a function of chloride concentration ($[HNO_3]$ = 0.2 mol L^{-1} (○) and 1 mol L^{-1} (●)), and (b) as a function of nitrate concentration ($[Cl^-]$ = 2 mmol L^{-1}).

TABLE 1: Reactions and Rate Constants Used for Modeling[a]

reaction no.	reaction	k (L mol^{-1} s^{-1})	reference
13	$HNO_3 \rightarrow H^+ + NO_3^-$	2×10^{10} (s^{-1})	28,29
−13	$H^+ + NO_3^- \rightarrow HNO_3$	$(4.4 \text{ to } 6.0)^b \times 10^8$	30
7	$^\bullet OH + HNO_3 \rightarrow H_2O + NO_3^\bullet$	$(0.88 \text{ to } 1.2)^b \times 10^8$	10
−7	$NO_3^\bullet + H_2O \rightarrow HNO_3 + {}^\bullet OH$	3×10^2	10
1	$NO_3^\bullet + Cl^- \rightarrow NO_3^- + Cl^\bullet$	3.5×10^8	
−1	$NO_3^- + Cl^\bullet \rightarrow NO_3^\bullet + Cl^-$	1.0×10^8	5
10	$e_{aq}^- + NO_3^- \rightarrow NO_3^{\bullet 2-}$	9.7×10^9	31
10a	$NO_3^{\bullet 2-} + H^+ \rightarrow NO_2 + OH^-$	4.5×10^{10}	32
11	$e_{aq}^- + H^+ \rightarrow H^\bullet$	2.3×10^{10}	31
12	$H^\bullet + NO_3^- \rightarrow NO_2^\bullet + OH^-$	4.4×10^6	33
14	$H^\bullet + HNO_3 \rightarrow H_2 + NO_3^\bullet$	$\leq 1 \times 10^7$	*c*
9	$^\bullet OH + Cl^- \rightarrow HOCl^{\bullet-}$	4.3×10^9	14
−9	$HOCl^{\bullet-} \rightarrow {}^\bullet OH + Cl^-$	6.1×10^9 (s^{-1})	14
15	$HOCl^{\bullet-} + H^+ \rightarrow H_2O + Cl^\bullet$	2.1×10^{10}	14
−15	$Cl^\bullet + H_2O \rightarrow HOCl^{\bullet-} + H^+$	4.5×10^3	24
2	$Cl^\bullet + Cl^- \rightarrow Cl_2^{\bullet-}$	8.5×10^9	24,34,35
−2	$Cl_2^{\bullet-} \rightarrow Cl^\bullet + Cl^-$	6×10^4 (s^{-1})	24
3	$Cl_2^{\bullet-} + Cl_2^{\bullet-} \rightarrow 2Cl^- + Cl_2$	2×10^9	*d*, 17
16	$^\bullet OH + {}^\bullet OH \rightarrow H_2O_2$	5.5×10^9	31
17	$H^\bullet + {}^\bullet OH \rightarrow H_2O$	7×10^9	36
18	$H^\bullet + H^\bullet \rightarrow H_2$	7.8×10^9	31
19	$NO_3^\bullet + NO_2^\bullet \rightarrow N_2O_5$	1.0×10^9	37
20	$NO_2^\bullet + NO_2^\bullet \rightarrow N_2O_4$	4.7×10^8	38
21	$N_2O_4 \rightarrow NO_2^\bullet + NO_2^\bullet$	6.8×10^3 (s^{-1})	38
22	$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$	1.8×10^1	38
23	$^\bullet OH + NO_2^\bullet \rightarrow HONO_2$ or HNO_3	4.5×10^9	39
24	$H^\bullet + NO_2^\bullet \rightarrow HNO_2$	1×10^{10}	39
25	$NO_3^\bullet + NO_3^\bullet \rightarrow$ products	4×10^6	40
26	$^\bullet OH + NO_3^\bullet \rightarrow HONO_3$	1×10^{10}	*e*
27	$H^\bullet + NO_3^\bullet \rightarrow HNO_3$	1×10^{10}	*e*
28	$Cl_2^{\bullet-} + {}^\bullet OH \rightarrow HOCl + Cl^-$	1×10^{10}	20
29	$Cl_2^{\bullet-} + H^\bullet \rightarrow H^+ + 2Cl^-$	7×10^9	15
30	$NO_3^\bullet + Cl_2^{\bullet-} \rightarrow NO_3^- + Cl_2$	1×10^9	
31	$NO_2^\bullet + Cl_2^{\bullet-} \rightarrow (NO_2^- + Cl_2)$ or $(NO_2^+ + 2Cl^-)$	$\leq 1 \times 10^9$	

[a] The rate constants are given in second-order units, except where noted. [b] Depending on ionic strength, see ref 10. [c] See text. [d] This work. [e] Estimated from gas-phase value.[18]

Discussion

The present results indicate that the ionic strength effect is much lower than that reported previously and is probably negligible, more like the small effects noted previously for reactions of ions and neutral molecules.[8] We should point out that in preliminary experiments we did detect an effect of sodium perchlorate on the rate of reaction 1. This effect vanished when we purchased a high-purity sample of the salt. We suggest that the effect of ionic strength on the kinetics of $NO_3^\bullet$ reactions that was observed before[5] may be the result of impurities in the salts. The greater ionic strength effect observed in the earlier work[4,21] probably indicates also additional experimental complications,[5] and possibly including an effect of ionic strength on the reaction that is employed to generate $NO_3^\bullet$.

Reaction 30 may play an important role in atmospheric aerosols. It leads, along with reaction 1, to conversion of chloride ions into chlorine, which may diffuse from the acidic droplet into the gas phase and undergo UV photolysis. This reaction is similar to the known reaction between ozone and $Cl_2^{\bullet-}$, for which a rate constant of 9 × 10^7 L mol^{-1} s^{-1} in aqueous solutions has been reported.[22] Reaction 31, on the other hand, may proceed in two opposing directions, leading to oxidation or reduction of $Cl_2^{\bullet-}$, and its rate constant may be significant in atmospheric modeling despite its lack of effect on the current system.

Reduction Potential Calculations. The rate constant reported here, $k_1 = (3.5 \pm 0.5) \times 10^8$ L mol^{-1} s^{-1}, can be combined with the reported rate constant for the reverse reaction, $k_{-1} = 1.0 \times 10^8$ L mol^{-1} s^{-1}, to yield an equilibrium constant for the reaction of $NO_3^\bullet$ with Cl^-, $K_1 = (3.5 \pm 0.5)$. This leads to a value for the difference between the reduction potentials of these two radicals, $E°(NO_3^\bullet/NO_3^-) - E°(Cl^\bullet/Cl^-) = 0.032 \pm 0.005$ V. A reduction potential of $E°(Cl^\bullet/Cl^-) = 2.41$ V has been calculated before[23] from the reduction potential $E°({}^\bullet OH/OH^-) = 1.89$ V and the equilibrium constants for reactions 9 and 13 as determined by Jayson et al.[14] By replacing the earlier value[14] of k_{-13} with the latest value[24] given in Table 1 and taking the latest recommended value[19] for $E°({}^\bullet OH/OH^-) = 1.90$ V, we calculate $E°(Cl^\bullet/Cl^-) = (2.44 \pm 0.01)$ V. This leads to $E°(NO_3^\bullet/NO_3^-) = (2.47 \pm 0.01)$ V. (The indicated uncertainty does not include the uncertainty in the value for the reference couple.)

In a previous study,[25] we had determined $E°(SO_4^{\bullet-}/SO_4^{2-}) - E°(Cl^\bullet/Cl^-) = 0.003$ V at near zero ionic strength. Because of round-off above, this leads to $E°(SO_4^{\bullet-}/SO_4^{2-}) = 2.45$ V. Studies of the forward and reverse reactions

$$SO_4^{\bullet-} + NO_3^- \rightleftarrows SO_4^{2-} + NO_3^\bullet \qquad (32)$$

found $k_{32} = 5.0 \times 10^4$ L mol^{-1} s^{-1} [4,26] and $k_{-32} = 1.0 \times 10^5$ L mol^{-1} s^{-1}.[26] The equilibrium constant, $K_{32} = 0.5 \pm 0.1$, leads to a reduction potential difference of 18 mV at an ionic strength of approximately 0.25 mol L^{-1}. Correcting the forward reaction to zero ionic strength gives $k_{32} = 2.1 \times 10^4$ L mol^{-1} s^{-1} and $K_{32} = 0.21 \pm 0.1$. From this we obtain $E°(NO_3^\bullet/NO_3^-) - E°(SO_4^{\bullet-}/SO_4^{2-}) = 0.040 \pm 0.015$ V and $E°(NO_3^\bullet/NO_3^-) = 2.49 \pm 0.02$ V.

This value is confirmed by the less precise value of $E°(NO_3^\bullet/NO_3^-) - E°(SO_4^{\bullet-}/SO_4^{2-}) = 0.031 \pm 0.029$ V, which can be

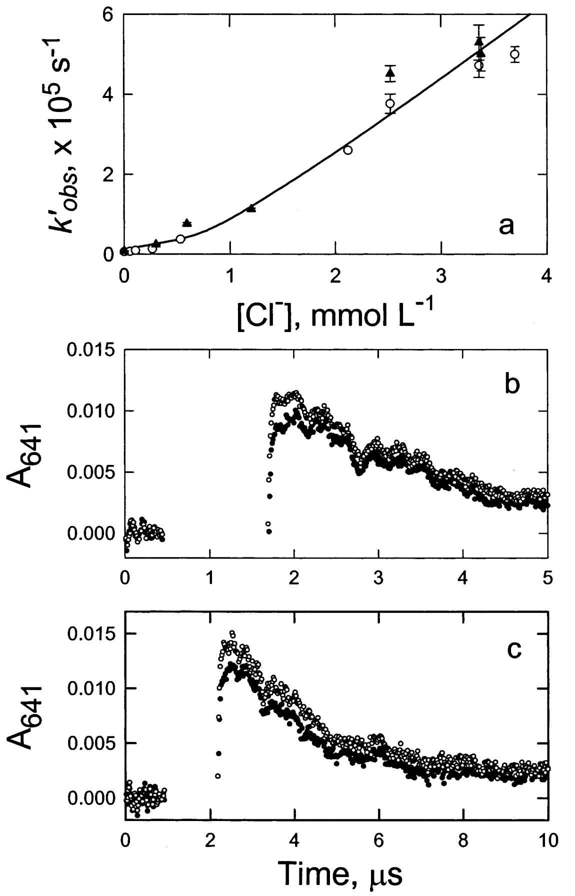

Figure 5. Effect of ionic strength: (a) the observed rate of decay of the absorbance at 641 nm (nitrate radicals) as a function of chloride ion concentration in 0.2 mol L^{-1} HNO_3 solutions in the absence (○) and presence (●) of 2 mol L^{-1} $NaClO_4$; (b) and (c) typical comparative traces at 1.2 and 2.5 mmol L^{-1} Cl^-, respectively, in the absence (○) and presence (●) of 2 mol L^{-1} $NaClO_4$.

derived from equilibrium measurements on the reactions

$$ClO_3^{\bullet} + NO_3^- \rightleftarrows ClO_3^- + NO_3^{\bullet} \qquad (33)$$

and

$$SO_4^{\bullet -} + ClO_3^- \rightleftarrows SO_4^{2-} + ClO_3^{\bullet} \qquad (34)$$

as discussed in our previous paper.[10] This leads to $E°(NO_3^{\bullet}/NO_3^-) = 2.48 \pm 0.03$ V.

In a recent study[10] we had determined the equilibrium constant for the reaction

$$^{\bullet}OH + HNO_3 \rightleftarrows H_2O + NO_3^{\bullet} \qquad (7)$$

from the forward and reverse rate constants. The rate constants at zero ionic strength were found to be $k_7 = (8.6 \pm 1.3) \times 10^7$ L mol^{-1} s^{-1} and $k_{-7} = (3 \pm 1) \times 10^2$ L mol^{-1} s^{-1}, and the equilibrium constant $K_7 = (2.8 \pm 0.4) \times 10^5$. From the latter value of K_7 and taking $E°(H^+,{}^{\bullet}OH/H_2O) = 2.72$ V we calculated a reduction potential $E°(NO_3^{\bullet}/NO_3^-) = (2.48 \pm 0.01)$ V. In this calculation, however, we failed to notice that $E°(H^+,{}^{\bullet}OH/H_2O) = 2.72$ V is derived from $E°({}^{\bullet}OH/OH^-) = 1.90$ V by taking $K_w = 10^{-14}$ and not taking into account the concentration of water as 55.56 mol L^{-1} (i.e., taking the standard state of liquid water as 1 rather than taking the activity of water). Since our value of $K_7 = (2.8 \pm 0.4) \times 10^5$ includes the activity of water (to obtain a dimensionless equilibrium constant), our previous calculation had mixed different standard states and was incorrect. The correct calculation that can be based on $E°(H^+,{}^{\bullet}OH/H_2O) = 2.72$ V should take the rate constant of the reverse reaction in first-order units, $k_{-7} = (1.7 \pm 0.6) \times 10^4$ s^{-1}, and $K_7 = (5.0 \pm 1.5) \times 10^3$ L mol^{-1}, to yield a reduction potential of $E°(NO_3^{\bullet}/NO_3^-) = (2.58 \pm 0.02)$ V.

This corrected value is higher than the three values derived above from the various other equilibria. Those three values were based directly or indirectly on $E°(Cl^{\bullet}/Cl^-) = (2.44 \pm 0.01)$ V and are self-consistent at $E°(NO_3^{\bullet}/NO_3^-) = (2.48 \pm 0.03)$ V. The value of $E°(NO_3^{\bullet}/NO_3^-) = (2.58 \pm 0.02)$ V is based directly on $E°(H^+,{}^{\bullet}OH/H_2O) = 2.72$ V. The discrepancy between these two sets of values raises doubts about the value of the equilibrium constant for the system of $Cl^{\bullet}$ vs ${}^{\bullet}OH$ or $NO_3^{\bullet}$ vs ${}^{\bullet}OH$ or both. Indeed, inspection of the equilibria in Table 1 shows that K_{15} should be equal to $K_7K_1/(K_9K_{13})$. The values in Table 1, however, show a discrepancy of a factor of about 100, which translates to a reduction potential difference of about 0.1 V, as above. Since the rate constants for reactions of ${}^{\bullet}OH$ radicals with nitrate and chloride ions are relatively high and have been measured with sufficient accuracy, we expect that the discrepancy in reduction potentials is due to uncertainties in the rate constants for the slow reactions of $Cl^{\bullet}$ and $NO_3^{\bullet}$ with water. The slowness of these reactions also means that the discrepancy will have little impact on the kinetic model, since these reactions have little effect on the time history of the $NO_3^{\bullet -}$ or $Cl_2^{\bullet -}$. Literature values for the kinetics of the reactions of $Cl^{\bullet}$ and $NO_3^{\bullet}$ with water vary widely, particularly for $NO_3^{\bullet}$. Moreover, the reactions of these radicals with water may not produce ${}^{\bullet}OH$ directly; at least for the case of $Cl^{\bullet}$ the reaction has been suggested to produce an adduct which involves additional equilibria on route to formation of ${}^{\bullet}OH$.[24,27] We believe that further measurements are necessary to reconcile the reduction potentials discussed above. In the meantime, however, because of smaller discrepancies between experimental results by various authors on the Cl systems, as compared with wider discrepancies on the ${}^{\bullet}OH/NO_3^{\bullet}$ system, we tentatively adopt the value of $E°(NO_3^{\bullet}/NO_3^-) = (2.48 \pm 0.03)$ V.

References and Notes

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