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Oxidation of Ferrous Ions by Ozone in Acidic Solutions

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The oxidation of ferrous ions by ozone in acidic solutions of pH 0–2 was studied using a stopped-flow spectrophotometer. The reaction can be characterized as an oxygen atom transfer from O_3 to Fe^{2+}. An intermediate product assigned to be the ferryl ion, FeO^{2+}, was found and its UV–vis spectrum measured. A reaction mechanism is proposed, which accounts for all our experimental results. Accordingly, the ferryl ion is formed by $Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2$ with a rate constant $k = (8.2 \pm 0.3) \times 10^5\ M^{-1}\ s^{-1}$. With an excess of Fe^{2+}, the reaction $FeO^{2+} + Fe^{2+} \xrightarrow{2H^+} 2Fe^{3+} + H_2O$, $k = (1.4 \pm 0.2) \times 10^5\ M^{-1}\ s^{-1}$, is dominant in the decay of FeO^{2+}, thus yielding the stoichiometric ratio $\Delta[O_3]/\Delta[Fe^{2+}] = 0.5$ for $[Fe^{2+}]_0/[O_3]_0 \geq 3$. With an excess of O_3, the decay is governed by the following set of reactions: $FeO^{2+} \xrightarrow{H_2O} Fe^{3+} + OH + OH^-$, $k = (1.3 \pm 0.2) \times 10^{-2}\ s^{-1}$; $FeO^{2+} + OH \rightarrow Fe^{3+} + HO_2^-$, $k = (1.0 \pm 0.5) \times 10^7\ M^{-1}\ s^{-1}$; $FeO^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO_2 + OH^-$, $k = (1.0 \pm 0.1) \times 10^4\ M^{-1}\ s^{-1}$; $FeO^{2+} + HO_2 \rightarrow Fe^{3+} + O_2 + OH^-$, $k = (2.0 \pm 1.0) \times 10^6\ M^{-1}\ s^{-1}$. No evidence could be obtained for the ferryl ion reacting with ozone, $k < 5\ M^{-1}\ s^{-1}$, or itself, $k < 50\ M^{-1}\ s^{-1}$.

Introduction

In the aqueous phase of the atmosphere (aerosols, clouds, fog, etc.), where iron,[1] acids, and ozone are simultaneously present,[2–5] the oxidation of Fe^{2+} by O_3 is very important as an ozone sink. This reaction has been extensively studied[6–11] as a major reaction in waste water ozonation and in analytical chemistry for quantitative determination of O_3.

In spite of the effort put into its study, discrepancies as to mechanism, stoichiometry, and rate constant of the reaction are still unresolved. The second-order rate constant of ferrous ion oxidation by ozone was found to exceed the $5 \times 10^5\ M^{-1}\ s^{-1}$ value of Hoigné et al.,[9] who in their paper support a single electron transfer mechanism, producing the OH radical directly. In a later study,[12] they proved that no OH radicals were formed directly and they suggested a ferryl ion formation as an intermediate. On the other hand, Conocchioli et al.[6] give a rate constant of $1.7 \times 10^5\ M^{-1}\ s^{-1}$ and postulate the formation of 40% ferryl ion and 60% OH radical. Tyupalo et al.[7,8] support the OH-producing mechanism and a constant stoichiometric ratio, $\Delta O_3/\Delta Fe^{3+} = 0.5$, when $[Fe^{2+}]_0 \gg [O_3]_0$. This mechanism and stoichiometry is also supported by Hart et al.[13] Under conditions of excess Fe^{2+}, Yang and Neely[10] get a time-dependent $\Delta O_3/\Delta Fe^{3+}$ stoichiometric ratio ranging from 0.54 to 0.4 (15 min), depending on a pH from 1.3 to 5.4 and on the initial Fe^{2+} and O_3 concentrations. In a more recent paper,[11] however, these authors use the ferrous–ozone system as a means of an indirect analytical determination of O_3 concentration in water, using a stoichiometric ratio of 0.5 at pH 2. Another work,[14] proposing the intermediacy of a complex suggested to be the ferryl ion in the oxidation of Fe^{2+} by ozone in acidic solution has come to our attention during the preparation of this manuscript.

Although the ferryl ion intermediate has been proposed in the Fenton reaction, direct OH formation from $H_2O_2 + Fe^{2+}$ seems to be the most generally accepted mechanism,[15–17] especially at low pH.[18,19] Despite this, the ferryl ion intermediate is commonly proposed in reactions of Fe^{2+} complexes with H_2O_2, for example nucleotide complexes,[20] porphyrin complexes,[21–23] and EDTA complexes[24,25] and in the reaction of H_2O_2 with Fe^{2+} in the presence of organic substrates.[26] Furthermore, the kinetic, spectral, and chemical properties of ferryl and ferryl pyrophosphate complexes in alkaline solution have been explored by pulse radiolysis.[27–29] Thus the existence of the ferryl ion has quite recently become accepted. It has been produced photochemically from an anaerobic mixture of flavin mononucleotide, H_2O_2, and an iron chelate[30] and synthetically as ferryl porphyrin complexes.[31]

The purpose of this study is to elucidate the mechanism of the oxidation of Fe^{2+} by ozone in acidic solution, determine the rate

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constants, and investigate the possible intermediacy of a ferrous–ozone complex likely to be the ferryl ion (the ferryl ion has a formal oxidation state of +4 [32]).

Experimental Section

Materials. All solutions were prepared using triply-distilled water. $(NH_4)_2Fe(SO_4)_2$ (maximum 0.002% Mn), $NH_4Fe(SO_4)_2$, and H_2SO_4 (Merck pa) and $HClO_4$ doubly vacuum distilled from Vycor and $Fe(ClO_4)_2$ (Frederik Smith Chem. Co) were used as supplied. Concentrated gaseous ozone was prepared as described elsewhere.[13,33] An aqueous stock solution in 0.01, 0.1, or 1 M $HClO_4$ or 0.4 M H_2SO_4 was prepared daily by transferring about 20 mL of ozone gas into a 100-mL syringe containing 70 mL of acid, shaking, and expelling the excess gas. This procedure gave ozone stock concentrations of about 4×10^{-3} M. To avoid photochemical decomposition, handling of O_3 solutions was carried out in a dimly lit room. The 1 M $HClO_4$ and 0.4 M H_2SO_4 ozone stock solutions remain stable throughout a working day, while 0.1 and 0.01 M $HClO_4$ solutions are somewhat less stable. Unless otherwise specified, $(NH_4)_2Fe(SO_4)_2$ was used as the source of Fe^{2+}.

Apparatus. A Hi-Tech SF-51 stopped-flow spectrophotometer (SFS) with UV and vis lamps was used. This instrument has a dead (mixing) time of about 1 ms, which enables us to measure rate constants in the order of 700 s^{-1}. Either 0.2- or 1-cm quartz cells were thermostated at 25.0 ± 0.1 °C. The data were recorded and analyzed on an on-line Apple IIe computer with Hi-Tech software. The reaction was studied in the UV and visible wavelength range, 200–500 nm, in the time range 0.001–400 s. Prior to every experiment, the ozone drive-syringe was refilled with fresh solution from the reservoir-syringe. The thermal decomposition of O_3 in the stopped-flow cell ($((1-2) \times 10^{-4}$ M O_3 in 1 M $HClO_4$) did not exceed 3% over a 400-s time span and was thus negligible.

An alternative "rapid-mixing device" (RMD) was used to measure O_2 formation during the ferrous–ozone reaction and to determine H_2O_2–FeO^{2+} stoichiometry. It consists of two 100-mL glass syringes that are driven simultaneously by a motor. Their content is mixed through a Y-joint. A mixing time of about 0.5 s was estimated for the RMD. The flow mixing-rate could be varied in the 0.2–10 mL s^{-1} range, but the value typically used was 2.4 mL s^{-1}. A constant-volume mixing ratio of 1:1 was established in both stopped-flow techniques.

O_2 Measurements. Oxygen was measured by an oxygen electrode, a TCM 1 TC Oxygen Monitor from the Radiometer Corp. The electrode was coupled to the RMD through a Teflon flow cell. This setup was calibrated using O_2-free and O_2-saturated solutions. Although this type of oxygen monitor is not designed for fast reaction kinetics, we found its 95% response time to be 5 s, which was satisfactory for our purposes. By using argon saturated solutions of 4.0×10^{-4} M Fe^{2+} and 3.82×10^{-4} M O_3 and mixing them in the RMD, the O_2 content of the reaction mixture was monitored starting about 2 s after mixing. The O_2 content of each reactant solution was then measured separately and the O_2 generated during the reaction obtained as the difference.

O_3 Measurements. Ozone concentration was measured spectrophotometrically at its maximum absorption wavelength, $\lambda_{max} = 260$ nm, using an extinction coefficient of $\epsilon_{260} = 3300$ M^{-1} cm^{-1}.[13] When ozone was measured for stoichiometric determinations, the absorbance of the reaction mixture (effluent in a 10-mL syringe) was measured at selected time intervals after mixing (30, 120, 400, or after 600 s). Then the effluent was bubbled, at selected times after mixing, with Ar gas at a flow rate of about 14 mL s^{-1} for 5 min to flush excess O_3 from the effluent.[34] The Ar-gas stream was passed through a washing bottle containing 1 M $HClO_4$ before entering the effluent. This bubbling procedure proved effective for removing excess O_3 at least within the detection limit of 0.5×10^{-6} M O_3. The absorbance of the effluent after flushing was measured, and the difference between the absorbance before and after yielded the amount of unreacted O_3 at the selected time after mixing.

Fe^{3+} Measurements. Fe^{3+} concentration was determined spectrophotometrically at $\lambda_{max} = 238$ nm using $\epsilon_{238} = 4230$ M^{-1} cm^{-1}.[35] At 260 nm, where $[O_3]$ is monitored, the extinction coefficient of Fe^{3+} is $\epsilon(Fe^{3+})_{260} = 2950$ M^{-1} cm^{-1}.[35]

H_2O_2 Measurements. The concentration of hydrogen peroxide was determined by mixing equal volumes of the argon-flushed effluent with 10^{-2} M Fe^{2+} in 1 M $HClO_4$ and letting this mixture react for about 1 min and measuring the absorbance at 238 nm. After subtraction of the absorbance of the blank solution, 5×10^{-3} M Fe^{2+}, the concentration of Fe^{3+} was calculated. The excess Fe^{3+} concentration thus measured divided by half the Fe^{3+} concentration measured in the argon-flushed effluent equals the concentration of H_2O_2 in the effluent.

Computer Simulations. All our experiments were modeled using Chemsimul,[37] a program developed at RISØ for numerical simulation of chemical reaction systems, and its input files.[38] This ensures a modeling based on an exhaustive set of radical reactions in water, in addition to the reactions describing the subject of interest, in this case the ferrous–ozone system. Thus a total of more than 50 water radical reactions and their rate constants[38] were included in the model, regardless of their influence on the subject studied. In this way three rate constants of the ferrous–ozone system and the spectrum of FeO^{2+} have been determined (see below).

Results

Experiments with $[O_3]_0 \geq [Fe^{2+}]_0$. Studying the ferrous–ozone system when $[O_3]_0 \geq [Fe^{2+}]_0$ by stopped-flow at 260 nm ($\epsilon(O_3)_{260} = 3300$ M^{-1} cm^{-1} [13] and $\epsilon(Fe^{3+})_{260} = 2950$ M^{-1} cm^{-1} [35,36]) allowed observation of two distinct kinetic steps in the time range 0.001–400 s (Figure 1A,B).

The rapid decay step (time span 1–50 ms; Figure 1A) is O_3 and Fe^{2+} concentration dependent and of first-order, while the slower buildup step (time span ≃ 50 ms–400 s; Figure 1B) is mixed-order and independent of O_3 in the concentration range $(0.05–0.4) \times 10^{-3}$ M. At 320 nm, where the extinction coefficients of Fe^{3+} and O_3 are practically zero (Figure 7), a kinetically equivalent but reversed picture is observed, a fast buildup followed by a slow decay (Figure 1C,D). The presence of these two distinct steps is evidence for the formation of an intermediate, prior to the formation of ferric ion as the final product. The first step may be ascribed to reaction 1, and the 0.05–400-s buildup step

$$Fe^{2+} + O_3 \rightarrow FeO_3^{2+} \quad (Fe(IV)) \qquad (1)$$

to Fe^{3+} ion formation is a result of the decay of the intermediate species. The spectrum resulting from initial conditions of $[O_3]_0 = [Fe^{2+}]_0$ is exclusively due to the ferric ion, while, in the case of initial ozone surplus, $[O_3]_0 > [Fe^{2+}]_0$, it is composed of the ferric ion and ozone spectra. Assuming the stoichiometry of one intermediate species formed per ozone used, the change in absorbance (Figure 1A) yields a roughly estimated extinction coefficient $\epsilon_{260} \approx 250$ M^{-1} cm^{-1} at 260 nm for the intermediate species. The intermediate species is formally iron in the oxidation state +4, Fe(IV), as the ferrous ion has been oxidized by two electron equiv.

From absorbance changes at 230, 260, and >305 nm, a rate constant $k_1 = (8.2 \pm 0.3) \times 10^5$ M^{-1} s^{-1} was determined under pseudo-first-order conditions with excess O_3, $[O_3]_0 = (0.35–4.0) \times 10^{-4}$ M, and $[Fe^{2+}]_0 = (0.2–1.0) \times 10^{-4}$ M at pH 0–2 in $HClO_4$ and in 0.4 M H_2SO_4 (Figure 2). This value is slightly higher than the lower value (5×10^5 M^{-1} s^{-1}), proposed by Hoigné,[9] but not in agreement with the values found by Conocchioli[6] and by Falcke[14] (1.7×10^5 M^{-1} s^{-1} and 2.3×10^5 M^{-1} s^{-1}, respectively). Within the uncertainty, a constant value of k_1 was obtained in the pH region 0–2 in $HClO_4$ and 0.4 M H_2SO_4. The formation of Fe^{3+} within the time span 0.05–400 s (Figure 1B) was independent of ozone concentration ($((0.05–0.4) \times 10^{-3}$ M O_3), and an upper limit of 5 M^{-1} s^{-1} can be estimated for the rate constant of any reaction between ozone and the intermediate species.

O_2 Formation for $[O_3]_0 \geq [Fe^{2+}]_0$. Measurements with the oxygen electrode yield the ratio of oxygen produced 5 s after

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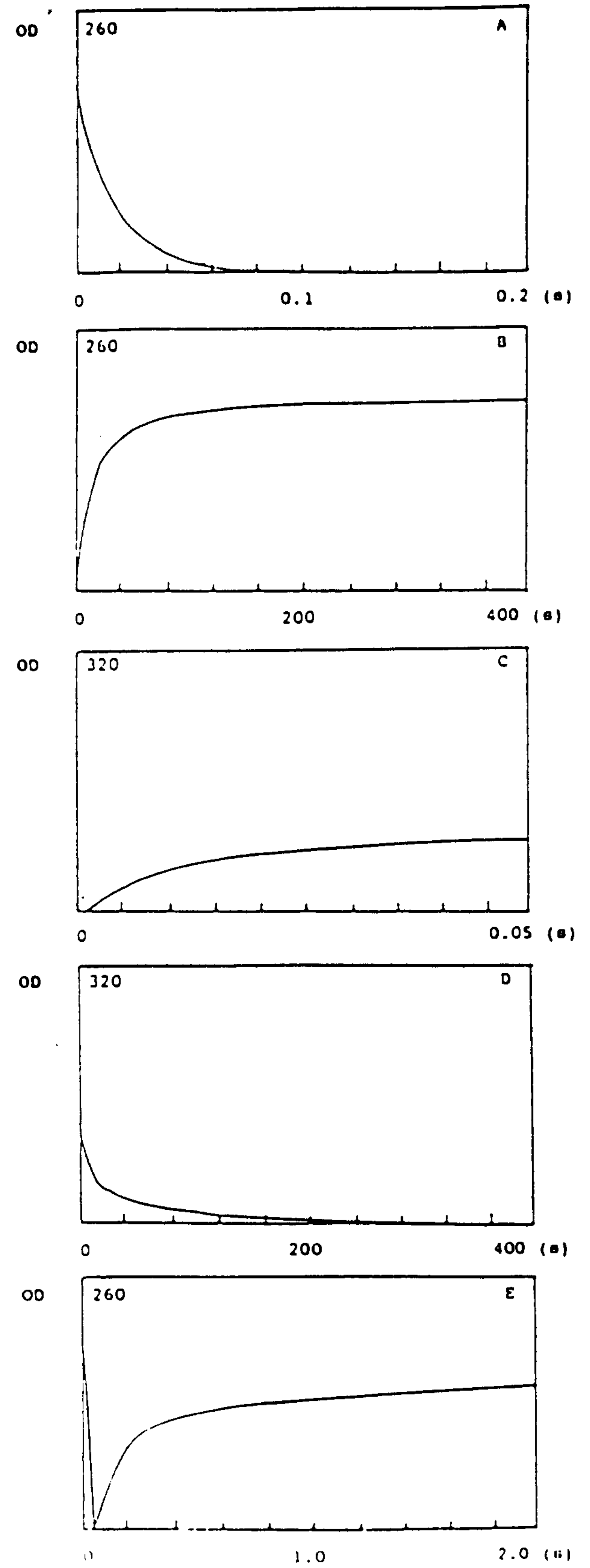

Figure 1. Characteristic kinetic traces at selected wavelengths with arbitrary absorbance (OD) scale: (A) $[Fe^{2+}]_0 = 5.0 \times 10^{-5}$ M, $[O_3]_0 = 1.26 \times 10^{-4}$ M, 260 nm; (B) $[Fe^{2+}]_0 = 1.0 \times 10^{-4}$ M, $[O_3]_0 = 1.0 \times 10^{-4}$ M, 260 nm; (C, D) $[Fe^{2+}]_0 = 1.1 \times 10^{-4}$ M, $[O_3]_0 = 1.3 \times 10^{-4}$ M, 320 nm; (E) $[Fe^{2+}]_0 = 1.0 \times 10^{-4}$ M, $[O_3]_0 = 6.0 \times 10^{-5}$ M, 260 nm.

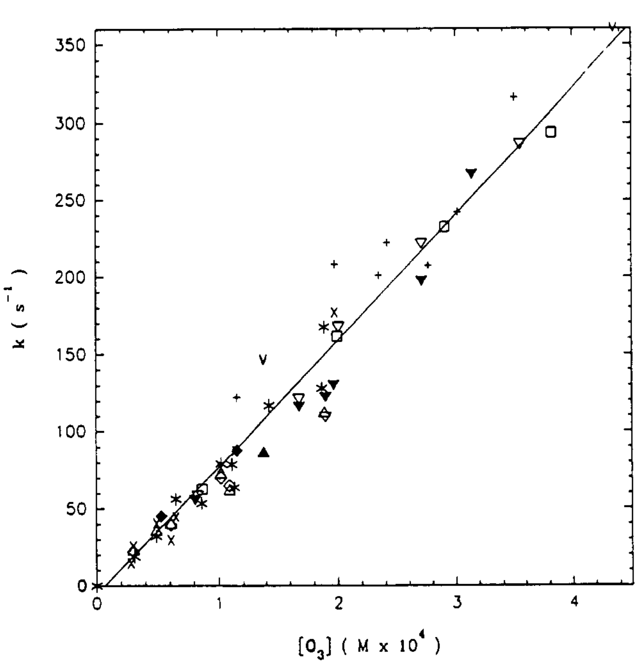

Figure 2. Apparent first-order rate constant k_2 versus $[O_3]_0$, where $[O_3]_0 \gg [Fe^{2+}]_0$, monitored as a decay at 260 nm ((∗) 1 M, (▽) 0.1 M, (□) 0.01 M $HClO_4$; (+) 0.4 M H_2SO_4) and as FeO^{2+} buildup at 230 ((X) 1 M $HClO_4$, (V) 0.4 M H_2SO_4), at 305 nm ((△) 1 M, (▼) 0.1 M $HClO_4$; (▲) 0.4 M, (♦) 0.04 M H_2SO_4) and at 335 nm ((◇) 1 M $HClO_4$). The solid line is the linear regression fit to the points, which gives $k_2 = (8.2 \pm 0.3) \times 10^5$ M^{-1} s^{-1}.

mixing equal concentrations of O_3 and Fe^{2+} per initial Fe^{2+} concentration, $[O_2]/[Fe^{2+}]_0 = 0.8$–0.9, which is close to unity. Due to the relatively fast reaction of the intermediate species with Fe^{2+} (reaction 3, below), about 30% of the initial Fe^{2+} has been converted to Fe^{3+}, 5 s after mixing. This would yield $[O_2]/[Fe^{2+}]_0 = 0.3$, if the reacted FeO_3^{2+} is assumed to be the only oxygen source. Therefore, we choose to designate the intermediate species in the reaction of ferrous ion with ozone, FeO^{2+} (reaction 2), rather than FeO_3^{2+} (reaction 1), and thus k_1 is replaced by k_2.

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \tag{2}$$

Experiments with $[Fe^{2+}]_0 \geq [O_3]_0$. With a small excess of Fe^{2+}, e.g. $[Fe^{2+}]_0/[O_3]_0 \simeq 1.2$, an additional buildup with time span 50–600 ms becomes evident (Figure 1E) between the fast decay and the slow buildup steps (Figure 1A,B). This additional buildup becomes more prominent when the initial ratio $[Fe^{2+}]_0/[O_3]_0$ is increased. At $[Fe^{2+}]_0/[O_3]_0 > 3$ it overshadows both the fast decay step and the slow buildup shown in Figure 1A,B, respectively, so that only an $[Fe^{2+}]$-dependent fast buildup measured at 260 nm, in the time range 5–100 ms, is observed. This buildup is ascribed to the reaction of the intermediate with Fe^{2+}:

$$FeO^{2+} + Fe^{2+} \xrightarrow{2H^+} 2Fe^{3+} + H_2O \tag{3}$$

The rate constant for reaction 3, $k_3 = (1.4 \pm 0.2) \times 10^5$ M^{-1} s^{-1}, was measured from the pseudo-first-order buildup of Fe^{3+} (Figure 1E) in $HClO_4$ solutions of pH 0–2 (λ = 230–260 nm, $[Fe^{2+}]_0 = (0.05$–$5.0) \times 10^{-3}$ M, and $[O_3]_0 = (0.002$–$0.04) \times 10^{-3}$ M; Figure 3).

As seen in Figure 3, the rate constant of reaction 3 in $HClO_4$ has a higher uncertainty at $0 \leq pH \leq 2$ than at pH = 0. A possible explanation for the deviations might be that the hydrated form of Fe^{3+}, $FeOH^{2+}$, of which 10% is present at pH = 2,[39,40] may have a small influence on the value of the absorbance 400–600 s after mixing (reaction has gone to completion) used to calculate the first-order rate constant.

$FeOFe^{4+}$ also called $Fe(OH)_2Fe^{4+}$ could be considered as an intermediate in reaction 3. This species is reported to have a broad absorption band in the UV–vis range (ϵ_{335} = 3000 M^{-1}

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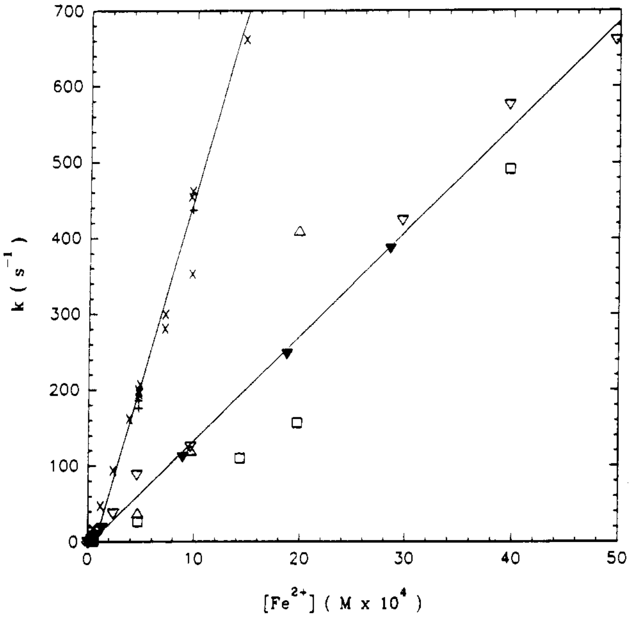

Figure 3. Apparent first-order rate constant k_3 versus $[Fe^{2+}]_0$, where $[Fe^{2+}]_0 \gg [O_3]_0$, monitored as a buildup of Fe^{3+} at 230 nm ((×) 0.4 M H_2SO_4) and at 260 nm ((▽) 1 M, (□) 0.1 M, (△) 0.01 M $HClO_4$, (+) 0.4 M H_2SO_4, and (▼) 1 M $HClO_4$ using $Fe(ClO_4)_2$). The lines are the linear regression fits to the $HClO_4$ and H_2SO_4 experiments, giving $k_3 = (1.4 \pm 0.2) \times 10^5$ M^{-1} s^{-1} and $k_3 = (4.6 \pm 0.5) \times 10^5$ M^{-1} s^{-1}, respectively.

cm^{-1}[6] or ϵ_{335} = 3400 M^{-1} cm^{-1}[41]) in 0.1–3.0 M perchloric acid. We do not observe any substantial transient absorption at 335 nm in our system when $[Fe^{2+}]_0 \gg [O_3]_0$. However, when we studied the system under the same conditions as Conocchioli et al.[6] (λ = 335 nm, 5 × 10^{-2} M Fe^{2+}, and 7.8 × 10^{-5} M O_3 in 1 M $HClO_4$) using $Fe(ClO_4)_2$ as our Fe^{2+} source, we get a transient absorption equal to 2.2 × 10^{-5} M $FeOFe^{4+}$ (using ϵ_{335} = 3000 M^{-1} cm^{-1}), corresponding to 30% of the FeO^{2+}. This transient has a decay rate close to 2.5 s^{-1}, in agreement with the dissociation rate for $FeOFe^{4+}$; $k = (k_1 + k_2 \times [H^+])$, where k_1 and k_2 equal 0.42 s^{-1} and 3.3 M^{-1} s^{-1}[42] or 0.35 s^{-1} and 3.5 M^{-1} s^{-1},[6,41,43] respectively. A possible explanation why we do not observe this transient when using $(NH_4)_2Fe(SO_4)_2$ is that as $FeOFe^{4+}$ decays, a ferric sulfate complex builds up, leaving practically no absorption difference (only 0.004) during the $FeOFe^{4+}$ decay time but leaving a permanent absorption due to some $FeSO_4^+$ (if using $\epsilon_{335} \approx 1100$ M^{-1} cm^{-1}, it corresponds to 66% of the FeO^{2+} yield in 5 × 10^{-2} M Fe^{2+}). The same experiment was carried out using only 1.0 × 10^{-3} M $(NH_4)_2Fe(SO_4)_2$ (maximum 0.002% Mn) and 6.0 × 10^{-5} M O_3 in 1 M $HClO_4$; here the transient was observed although only by 17% of the FeO^{2+} yield, and practically no permanent absorption due to the sulfate complex was seen. By comparison an experiment using 1.0 × 10^{-3} M $Fe(ClO_4)_2$ solution and otherwise identical conditions yielded 30% $FeOFe^{4+}$. Thus, we observe a transient at 335 nm identical to what Conocchioli et al. observe (although with a lower yield) when we reproduce their experimental conditions, but when we use $(NH_4)_2Fe(SO_4)_2$, the formation of the dimer is less pronounced and in large Fe^{2+} concentrations becomes overshadowed by the ferric sulfate complex. The formation of the dimer $FeOFe^{4+}$ occurs only under conditions of excess Fe^{2+} concentrations and thus can only have an influence on the determination of the rate of reaction 3. Since both $Fe(ClO_4)_2$ and $(NH_4)_2Fe(SO_4)_2$ give the same rate constant in $HClO_4$ (as opposed to the rate in H_2SO_4; see below), the influence is negligible. Falcke[14] did observe an absorbance at 335 nm but with a much lower extinction. He argued that no substantial amount of the dimer was formed.

Our experiments in 0.4 M H_2SO_4 ($k_3 = (4.6 \pm 0.5) \times 10^5$ M^{-1} s^{-1}; Figure 3) yield a distinctly higher rate constant than in $HClO_4$. This higher value may be due to a ferryl sulfate complex in analogy with the ferric sulfate complex formation (Fe^{2+} does not form a complex with the sulfate ion).[13,44]

When $[Fe^{2+}]_0/[O_3]_0 \geq 3$, the stoichiometric ratio $\Delta[O_3]/\Delta[Fe^{3+}] = 0.50 \pm 0.02$ was determined (400–600 s after mixing). This ratio is consistent with reactions 2 and 3 and is in accordance with the stoichiometry reported in the literature,[7,8,11,13] except by Yang et al.,[10] who reported a time-dependent ratio which remains constant at $\Delta[O_3]/\Delta[Fe^{3+}] = 0.4$ after 15 min, a finding which we are unable to reproduce.

Decay of the Intermediate FeO^{2+} Species. The decay of FeO^{2+} was monitored both in the 240–280-nm range (as a buildup of Fe^{3+}) and in the 200–230- and 280–350-nm range (as a decay of FeO^{2+}). Although the absorption change is much lower in the 280–350-nm range than in the 240–280-nm range, it is still more convenient to observe the intermediate species, FeO^{2+} in the former, higher wavelength region, where it is the predominating absorbing species. To get the optimal conditions for monitoring the decay reaction of FeO^{2+} (i.e. the longest half-life), it is convenient to start with equal reactant concentrations. The reaction expected to occur under these conditions, after the rapid formation of the intermediate, would be the FeO^{2+} self-reaction, in analogy with that of the ferryl pyrophosphate complex:[28]

$$2FeO^{2+} \rightarrow (FeOOFe^{4+}) \xrightarrow{H_2O} 2Fe^{3+} + OH^- + HO_2^- \quad (4)$$

The intermediate complex $FeOOFe^{4+}$ assumed, if formed at all, is rapidly hydrolyzed to Fe^{3+} and hydrogen peroxide.[28] However, the buildup kinetics (240–280 nm) and the decay kinetics (200–230 and 280–350 nm) observed are both of mixed order, but fairly close to first order, similar to the behavior of the ferryl complex in alkaline solution,[29] but with a different rate constant. Increasing the starting concentrations of both reactants ($[Fe^{2+}]_0 = [O_3]_0$ = (0.25–2.0) × 10^{-4} M in 1 M $HClO_4$) did not increase the rate of Fe^{3+} formation or the rate of decay of FeO^{2+}. The failure to observe any second-order kinetics suggests an upper limit of 50 M^{-1} s^{-1} for the rate constant of reaction 4.

As mentioned above, the decay of FeO^{2+} is not influenced by a surplus of ozone. The stoichiometric ratio $\Delta[O_3]/\Delta[Fe^{3+}]$, however, increases with increasing O_3 concentration at fixed Fe^{2+} concentration. At equal amounts of O_3 and Fe^{3+}, all the ozone is consumed and all Fe^{2+} is oxidized to Fe^{3+}. When the initial ratio $[O_3]_0/[Fe^{2+}]_0$ increases, $\Delta[O_3]/\Delta[Fe^{3+}]$, as measured 30–400 s after mixing, also increases (Figure 4). An increase to a stoichiometric ratio of about 1.5 is obtained when $[O_3]_0/[Fe^{2+}]_0$ increases from 0.5 to about 2–3. A further increase to a ratio of about 2.5 is obtained when the $[O_3]_0/[Fe^{2+}]_0$ ratio is increased further, from 3 to 13–14. The enhancement of O_3 destruction reflected by these ratios indicates a slow chain decomposition of O_3 caused by radicals (OH and/or HO_2), formed during the decay of FeO^{2+}.

As a consequence of this slow chain decomposition of ozone, the value of the stoichiometric ratio, $\Delta[O_3]/\Delta[Fe^{2+}]$, should depend on the time elapsed between mixing and stopping the reaction by expelling O_3 with argon. Indeed, stoichiometric ratios at different initial ratios $[O_3]_0/[Fe^{2+}]_0$ consistently increase with time elapsed (30, 120, 400, and 600 s; Table I).

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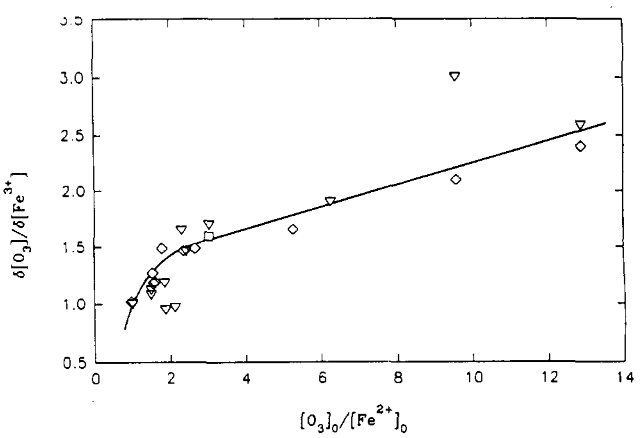

Figure 4. Stoichiometric ratios of ozone used per ferric ion produced, $\Delta[O_3]/\Delta[Fe^{3+}]$, as a function of the ratio of initial concentrations of ozone and ferrous ion, $[O_3]_0/[Fe^{2+}]_0$. Points are experimental results in 1 M $HClO_4$ obtained 120–160 (◇) and 300–400 (▽) s after mixing and in 0.01 M $HClO_4$ 400 (□) s after mixing. The solid line is a fit to the points found by modeling the conditions according to the proposed mechanism.

Reaction of H_2O_2. H_2O_2 is known to be an intermediate which is formed and destroyed during the decay of Fe(IV) in alkaline pyrophosphate solutions.[28,29] There is a definite possibility that H_2O_2 is an intermediate in the ferrous–ozone system, although no H_2O_2 has been found as end product in our stopped-flow experiments. Therefore, it was of interest to study the reaction of FeO^{2+} with hydrogen peroxide (reaction 5). Having produced

$$FeO^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO_2 + OH^- \qquad (5)$$

HO_2 in reaction 5, we may postulate that it will react with FeO^{2+} as well according to reaction 6. To study this possibility, a solution

$$FeO^{2+} + HO_2 \rightarrow Fe^{3+} + O_2 + OH^- \qquad (6)$$

containing both hydrogen peroxide and ozone was mixed with a Fe^{2+} solution. The concentration of O_3 in the O_3/H_2O_2 reservoir solution was measured just prior to and after each experiment in order to monitor the O_3 degradation caused by H_2O_2. This degradation was found to be negligible in accordance with the low rate constant known for reaction 7, $k_7 \leq 10^{-2}$ M^{-1} s^{-1}.[34,35] With a half-life of about 600 s, reaction 7 can have only a negligible

$$O_3 + H_2O_2 \rightarrow HO_2 + OH + O_2 \qquad (7)$$

effect in our experiments of time span 5 s. Concentrations of $[O_3]_0 = (5–9) \times 10^{-5}$ M, $[H_2O_2]_0 = (0.5–1.0) \times 10^{-5}$ M, and $[Fe^{2+}]_0 = 5 \times 10^{-5}$ M ensure an immediate production of FeO^{2+} within the first few milliseconds, which can then in turn react with H_2O_2. Thus, any reaction between Fe^{2+} and H_2O_2 ($k \leq 50$ M^{-1} s^{-1}) can be ruled out. From the decay monitored at 320 nm, where the dominant absorbing species is FeO^{2+}, a rate constant was determined, $k_5 = (2.0 \pm 0.2) \times 10^4$ M^{-1} s^{-1} (Figure 5). This rate constant may have to be divided by 2 if reaction 6 proceeds sufficiently fast (see Discussion).

A set of experiments devised to study the H_2O_2–FeO^{2+} reaction were also performed. By means of the RMD a volume of solution containing FeO^{2+} and Fe^{3+} was injected into a stirred equal volume of 5.1×10^{-5} M H_2O_2 solution. Equal volumes of 2.3×10^{-5} M O_3 and 2.6×10^{-5} M Fe^{2+} solutions were used in the RMD syringes. To ensure total conversion of Fe^{2+} into FeO^{2+} and Fe^{3+}, the flow rate on the RMD was chosen to assure a contact time of 0.5 s before reaching the H_2O_2 solution. The resulting solution was then analyzed for Fe^{3+} produced and H_2O_2 consumed. The results thus found give $\Delta[H_2O_2]/[Fe^{2+}]_0 \approx 0.30$. Chemsimul simulations give 0.28 for this ratio. However, when the same experiments are modeled with a 60–40% distribution of reactions 8 and 2, respectively,[6] the ratio is found to be 0.10. These results sharply contradict the results of Conocchioli et al.[6] and Falcke,[14] rendering reaction 8 very unlikely. The modeling shows that the amount of Fe^{3+} formed just after mixing O_3 and Fe^{2+} (0.5 s) is invariant with changes in the mixing time (range 0.2–2.0 s) of the Fe^{2+}–O_3 mixture with H_2O_2 solutions. To show that H_2O_2 does not react with end products, a ferrous–ozone mixture was allowed to stand 10 min (to allow the FeO^{2+} to decompose according to the suggested mechanism) before the mixture was added to the H_2O_2 solution. As expected, no H_2O_2 was consumed in this case.

Table I. Values for the Stoichiometric Ratio $\Delta[O_3]/\Delta[Fe^{3+}]$ at 30, 120, 400, and >600 s after Mixing, as a Function of $[O_3]_0/[Fe^{2+}]_0$ in 1 M $HClO_4$, 0.01 M $HClO_4$, and 0.4 M H_2SO_4

$[Fe^{2+}]_0$ ($M \times 10^6$)	$[O_3]_0$ ($M \times 10^6$)	$[O_3]_0/$ $[Fe^{2+}]_0$ init	$\Delta[O_3]/\Delta[Fe^{3+}]$ seconds after mixing 30	120	400	>600
20	20	1.0	1.0			
51	51	1.0			1.0	
20	31	1.5		1.3		
51	77	1.5			1.1	
20	32	1.6		1.2		
51	79	1.6		1.2		
20	36	1.8		1.5		
107	198	1.8			1.2[a]	1.2[a]
113	198	1.9			1.0[a]	1.0[a]
116	248	2.1			1.0[a]	1.0[a]
109	255	2.3			1.6[a]	1.8[a]
52	122	2.4		1.5		
52	126	2.4			1.5	
20	53	2.6		1.5		
25	76	3.0			1.7	
25	76	3.0		1.6[b]		
100	420	4.2				1.2
55	242	4.4				1.3
25	131	5.2		1.7		
55	297	5.5	1.4[a]			1.7[a]
55	314	5.7	1.5[a]			1.8[a]
25	158	6.2			1.9	
50	430	8.7				1.9
25	239	9.6		2.1	3.0	
34	346	10.2				3.4
34	351	10.3	2.0[a]			
34	357	10.5	1.5[a]			4.7[a]
34	357	10.5	1.8[a]			4.4[a]
20	242	12.1				2.1
25	322	12.9		2.4	2.6	

[a] In 0.4 M H_2SO_4. [b] In 0.01 M $HClO_4$.

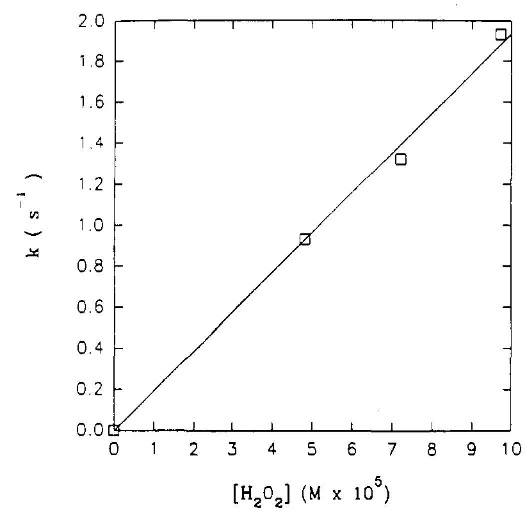

Figure 5. Apparent first-order rate constant for $H_2O_2 + FeO^{2+}$, with excess H_2O_2, monitored as FeO^{2+} decay at 320 nm (□) in 1 M $HClO_4$. The solid line is the linear regression fit to the points, giving $k_5 = (1.0$ ● $0.1) \times 10^4$ M^{-1} s^{-1} (the slope is divided by two due to reaction 6).

Spectrum of FeO^{2+}. To determine the spectrum of FeO^{2+}, the absorbance of a ferrous–ozone mixture ($[O_3]_0 = 1.3 \times 10^{-4}$ M and $[Fe^{2+}]_0 = 1.1 \times 10^{-4}$ M) in the time span 0.001–400 s was modeled according to the proposed mechanism. The time-de-

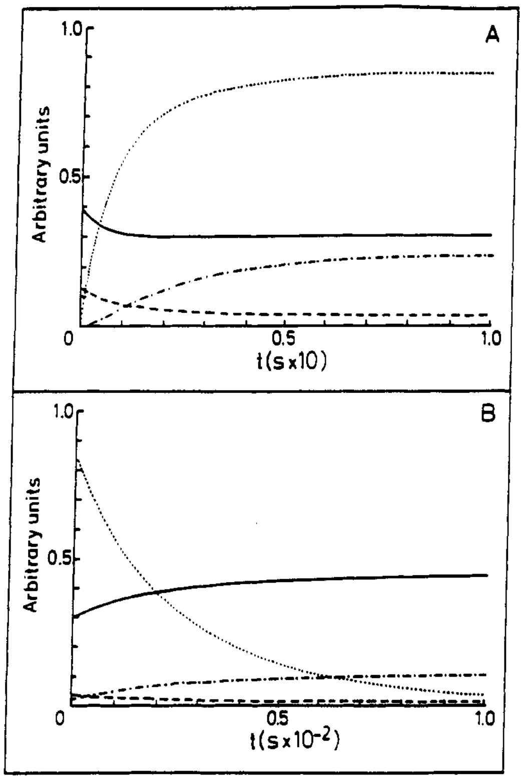

Figure 6. Computer simulation, based on the proposed mechanism, of the experimental absorbance observed at 250 nm in a mixture of 1.3 × 10^{-4} M O_3 and 1.1 × 10^{-4} M Fe^{2+} in 1 M $HClO_4$ as a function of time (—): (A) time-dependent (0–0.1 s) concentrations of $O_3 \times 10^3$ M (- - -), $Fe^{3+} \times 10^4$ M (-·-), and $FeO^{2+} \times 10^4$ M (···); (B) time-dependent (0–100 s) concentrations of $O_3 \times 10^3$ M (- - -), $Fe^{3+} \times 10^3$ M (-·-), and $FeO^{2+} \times 10^4$ M (···). These concentrations are used to calculate the extinction coefficients of FeO^{2+}. The stoichiometric ratio $\Delta[O_3]/\Delta[Fe^{3+}]$ is 1.1.

pendent concentrations of O_3, Fe^{3+}, FeO^{2+}, and the absorbance observed (Figure 6A,B) were calculated for each 10 nm in the λ range 200–350 nm. Since the concentration of FeO^{2+} reaches a plateau about 0.05 s after mixing, the modeled concentrations of O_3 and Fe^{3+} at 0.05 s (Figure 6A) and their respective extinction coefficients at selected wavelengths were used to subtract the O_3 and Fe^{3+} absorptions from the experimentally determined absorbance 0.05 s after mixing. As the extinction coefficients of Fe^{2+} and O_2 are negligible,[52,53] the remaining absorbance was ascribed to the intermediate species and converted into extinction coefficients by use of the modeled concentration of FeO^{2+} at 0.05 s. The FeO^{2+} spectrum thus obtained has a small broad peak around 300 nm and a continuum which grows in the UV as shown in Figure 7. Our spectrum is similar to that found by Falcke[14] but with lower extinction coefficients.

Discussion

The oxidation of Fe^{2+} by ozone proposed by Hart et al.[13] and by most of the other previous investigators[7-10] is initiated by the following reactions:

$$Fe^{2+} + O_3 \rightarrow Fe^{3+} + O_3^- \qquad (8)$$

$$O_3^- + H^+ \rightarrow OH + O_2 \qquad (9)$$

Here $k_8 = 1.7 \times 10^5$ M^{-1} s^{-1},[6] ≥ 5 × 10^5 M^{-1} s^{-1},[9] or = 2.3 × 10^5 M^{-1} s^{-1} [14] and $k_9 = (5–9) \times 10^{10}$ M^{-1} s^{-1}.[46,47] The OH produced in reaction 9 can then in turn react with any excess Fe^{2+} or O_3 available (reactions 10 and 12).

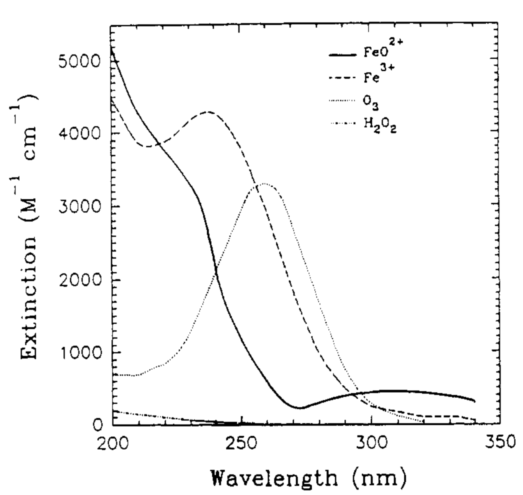

Figure 7. Extinction coefficients of FeO^{2+} found by computer modeling of experimental absorbencies in 1 M $HClO_4$. For comparison, the spectra of Fe^{3+}, O_3, and H_2O_2 in 1 M $HClO_4$ are also given.

Conocchioli et al.[6] and Falcke[14] found that reactions 8 and 9 were only partly in accordance with their results and proposed an intermediate species, Fe(IV), as in reaction 1 or 2. Nowell and Hoigné[12] also suggest such a species based on experiments in which they have shown that OH was not an immediate product of the ferrous–ozone reaction.

If reaction 8 were valid, then we should observe an immediate buildup of Fe^{3+} when mixing equal amounts of ozone and ferrous ion, as the rate of reaction 10, $k_{10} = 3 \times 10^8$ M^{-1} s^{-1},[48] is much

$$Fe^{2+} + OH \rightarrow Fe^{3+} + OH^- \qquad (10)$$

faster than the rate of reaction 2, making the latter rate-determining. In this case, every O_3 would produce two ferric ions (reaction 12 is negligible since $k = 1.1 \times 10^8$ M^{-1} s^{-1} [33]), which together have a higher total absorption at 260 nm than O_3 alone. Accordingly, an immediate increase in absorbance should be expected at 260 nm. Our experiments show however that this is not the case, as the buildup of Fe^{3+} is delayed by seconds when $[Fe^{2+}]_0 = [O_3]_0$ and the stoichiometric ratio of O_3 used per Fe^{3+} produced is still 1:1. This renders reaction 8 unnecessary and calls for an intermediate species, as in reaction 2.

Although the oxidation of ferrous by ozone may proceed through a simple addition reaction to produce FeO_3^{2+} (reaction 1), our oxygen measurements show immediate release of oxygen roughly corresponding to one O_2 released per O_3 consumed. As the initial step in the mechanism, we therefore propose the formation of an intermediate species designated FeO^{2+} (reaction 2), manifested in the rapid decay in absorbance (240–280 nm) and buildup (200–230 and 290–340 nm). This intermediate is likely to be the ferryl ion, Fe(IV), that may be ascribed one of the following two structures, e.g. $FeO^{2+} \equiv [Fe^{2+}(O) \leftrightarrow Fe^{4+}O^{2-} \leftrightarrow Fe^{3+}(O^{\bullet-})]$ or $Fe(OH)_2^{2+}$.

Our rate constant for reaction 2, $k_2 = (8.2 \pm 0.3) \times 10^5$ M^{-1} s^{-1}, is much higher than most previously published values, but it agrees with the lower limit value $k \geq 5 \times 10^5$ M^{-1} s^{-1} reported by Hoigné.[9] Conocchioli et al.[6] report a rate constant for reaction 2 of $(1.7 \pm 0.4) \times 10^5$ M^{-1} s^{-1}, which is based on their preliminary results on Fe^{3+} formation and $FeOFe^{4+}$ dissociation and therefore is more relevantly compared to our rate constant for reaction 3 in $HClO_4$, $k_3 = (1.4 \pm 0.2) \times 10^5$ M^{-1} s^{-1}, which designates the intermediate species reacting with Fe^{2+} forming Fe^{3+}. Thus, we find that, looking at the buildup (Figure 1E), reaction 3 will always be rate-determining compared to reaction 2 in the beginning of the reaction, since $k_3[Fe^{2+}] \leq k_2[Fe^{2+}]$, and what happens thereafter is dependent on the initial concentration ratio, $[O_3]_0/[Fe^{2+}]_0$. We cannot comment on the product distribution of $Fe^{3+}/FeOFe^{4+}$ found by Conocchioli et al. as we are unable to reproduce their results at 340 nm.[6] Falcke[14] has found a value

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for the rate constant, $k_2 = 2.3 \times 10^5$ M^{-1} s^{-1}; however, it is determined indirectly by computer calculations since the time resolution on his apparatus is too low to observe the fast decay that we attribute to reaction 2, directly.

The intermediate species, FeO^{2+}, reacts relatively fast with Fe^{2+} in $HClO_4$, $k_3 = (1.4 \pm 0.2) \times 10^5$ M^{-1} s^{-1}, forming Fe^{3+} ions (reaction 3) while maintaining the stoichiometric ratio, $\Delta[Fe^{3+}]/\Delta[O_3] = 2$, when $[Fe^{2+}]_0/[O_3]_0 > 3$. Falcke's rate constant, $k_3 = 3.8 \times 10^4$ M^{-1} s^{-1},[14] is a factor of 4 times lower than our k_3 in $HClO_4$. We can offer no explanation for this discrepancy. FeO^{2+} also reacts with H_2O_2, $k_5 = (1.0 \pm 0.1) \times 10^4$ M^{-1} s^{-1}, under the assumption that reaction 6 proceeds sufficiently fast (see later).

However, the above mentioned reactions are not sufficient to account for the decay of FeO^{2+} when $[O_3]_0/[Fe^{2+}]_0 \geq 1$. Since we have excluded second-order self-reactions of FeO^{2+} and the reaction with surplus ozone in pertinent time scales, we postulate that FeO^{2+} releases an OH radical in a first-order process according to

$$FeO^{2+} \xrightarrow{H_2O} Fe^{3+} + OH + OH^- \qquad (11)$$

as the only available alternative. This reaction is supported by the fact that when $[O_3]_0/[Fe^{2+}]_0 > 1$, the first-order rate constant determined as decay of FeO^{2+} is constant. OH-radical formation is also indicated by the slow chain decomposition of O_3, when O_3 is in surplus. The OH radical formed in reaction 11 may thus react with O_3 according to

$$O_3 + OH \rightarrow HO_2 + O_2 \qquad (12)$$

where $k_{12} = (1.1 \pm 0.2) \times 10^8$ M^{-1} s^{-1} [33] or with FeO^{2+} according to

$$FeO^{2+} + OH \rightarrow Fe^{3+} + HO_2^- \qquad (13)$$

When $[O_3]_0$ is close to $[Fe^{2+}]_0$, reaction 11 followed by reaction 13 is dominant, but when $[O_3]_0 \gg [Fe^{2+}]_0$, reaction 12 will interfere and destroy O_3 whereby the stoichiometric ratio increases. Reaction 13 produces HO_2^-/H_2O_2 ($pK_a = 11.7$), and this H_2O_2 may react with FeO^{2+} as shown in reaction 5, probably followed by reaction 6. A competing reaction for HO_2 is reaction 14, $k_{14} \leq 10^4$ M^{-1} s^{-1}.[33]

$$O_3 + HO_2 \rightarrow OH + 2O_2 \qquad (14)$$

Reactions 12 and 14 explain the observed chain decomposition of O_3 and, thus, the larger stoichiometric ratios observed when O_3 is in surplus. Ferric ions also react with HO_2/O_2^-. However, the rate constant $k \approx 2.5 \times 10^3$ M^{-1} s^{-1} [49] is so low that this reaction is insignificant in our experiments. Clearly, OH can react with other radicals and H_2O_2, but these reactions are too slow to be significant.

As reaction 11 is the rate-controlling step, k_{11} must be in the order of 10^{-2} s^{-1}, to account for the very slow decay of FeO^{2+} when $[O_3]_0 = [Fe^{2+}]_0$. The rate constants of reactions 6 and 13 are estimated from the results in Figure 4 in the following.

In the first part of the curve, the increase in $\Delta[O_3]/\Delta[Fe^{3+}]$ from 1 to about 1.5 as $[O_3]_0/[Fe^{2+}]_0$ increases from 1 to about 2–3 is consistent with the assumption that all of the OH radicals produced via reaction 11 are scavenged by the excess O_3, thus producing HO_2 radicals (reaction 12) which in turn react with FeO^{2+} (reaction 6) (k_{14} is probably much lower than k_6 at pH 0). On this basis, $k_{12} \geq 10k_{13}$; i.e., $k_{13} \leq 10^7$ M^{-1} s^{-1} is estimated.

To determine k_6, it is necessary to acknowledge that the HO_2 produced in reaction 5 might also attack excess O_3 (reaction 14, $k_{14} \leq 10^4$ M^{-1} s^{-1} [33]) or react through its dissociation product O_2^- ($pK_a = 4.8$) with a rate constant of 1.5×10^9 M^{-1} s^{-1}.[50] The overall rate constant $k_{14}(HO_2/O_2^-)$ at pH 0 is of the order 10^4 M^{-1} s^{-1}.

Table II. Reactions and Rate Constants Determined by Experimental Data and by Modeling of Experimental Data

reacn no.	reacn	rate constant
2	$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2$	$(8.2 \pm 0.3) \times 10^5$ M^{-1} s^{-1}
3	$FeO^{2+} + Fe^{2+} \xrightarrow{2H^+} 2Fe^{3+} + H_2O$	$(1.4 \pm 0.2) \times 10^5$ M^{-1} s^{-1}
4	$2FeO^{2+} \xrightarrow{H_2O} 2\ Fe^{3+} + OH^- + HO_2^-$	<50 M^{-1} s^{-1}
5	$FeO^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO_2 + OH^-$	$(1.0 \pm 0.1) \times 10^4$ M^{-1} s^{-1}
6	$FeO^{2+} + HO_2 \rightarrow Fe^{3+} + O_2 + OH^-$	$(2.0 \pm 1.0) \times 10^6$ M^{-1} s^{-1} [a]
11	$FeO^{2+} \xrightarrow{H_2O} Fe^{3+} + OH + OH^-$	$(1.3 \pm 0.2) \times 10^{-2}$ s^{-1} [a]
13	$FeO^{2+} + OH \rightarrow Fe^{3+} + HO_2^-$	$(1.0 \pm 0.5) \times 10^7$ M^{-1} s^{-1} [a]

[a] From modeling of experimental data.

The increased stoichiometric ratio $\Delta[O_3]/\Delta[Fe^{3+}]$, when $[O_3]_0/[Fe^{2+}]_0 > 2$–3, is rationalized in terms of competition between O_3 and FeO^{2+} for HO_2 radicals (reactions 6 and 14); thus, k_6 must be of the order of 10^6 M^{-1} s^{-1}, because its reaction rate should be at least 1 order of magnitude higher than that of reaction 14. Therefore, the rate constant of reaction 5 must be reduced by a stoichiometric factor of 2; i.e., $k_5 = (1.0 \pm 0.1) \times 10^4$ M^{-1} s^{-1}.

Both OH and HO_2 radicals formed in reactions 5 and 11, respectively, are able to initiate and carry the slow chain destruction of O_3 [51] (reactions 12 and 14), even after FeO^{2+} has totally disappeared. Accordingly, the increase in the stoichiometric ratio with time is largest at high $[O_3]_0/[Fe^{2+}]_0$ ratios and practically absent at $[O_3]_0/[Fe^{2+}]_0 \leq 2$–3.

Modeling of the proposed mechanism, reactions 2–7 and 10–14 (Table II) plus an exhaustive set of water radical reactions,[38] yielded the following best-fit values: $k_6 = (2.0 \pm 1.0) \times 10^6$ M^{-1} s^{-1}, $k_{11} = (1.3 \pm 0.2) \times 10^{-2}$ s^{-1}, and $k_{13} = (1.0 \pm 0.5) \times 10^7$ M^{-1} s^{-1}. The rate of reaction 11 dominates the first part of the decay curve at 340 nm when $[O_3]_0 = [Fe^{2+}]_0$, and the rate constant of reaction 13 is limited by competition with reaction 12, the chain decomposition of O_3. On the basis of the mechanism derived, computer modeling of all our stopped-flow experiments and the stoichiometric ratios yields good quality fits.

Conclusion

The rate constant found for ferryl ion formation, $(8.2 \pm 0.3) \times 10^5$ M^{-1} s^{-1}, is in agreement with an oxygen atom transfer from O_3 to Fe^{2+} producing FeO^{2+} and O_2. These findings support the calculations made by Bennett and Warlop,[54] which suggest that the rate constant should be in the range $(3$–$9) \times 10^5$ M^{-1} s^{-1}. The substitution of O_3 on Fe^{2+} takes place somewhat more rapidly than that of NO on Fe^{2+}, the latter being 6.2×10^5 M^{-1} s^{-1}.[55] Although a direct single-electron transfer (reaction 8) parallel to FeO^{2+} formation was suggested both with an excess of Fe^{2+} [6] and an excess of O_3,[14] we find no indication for such a transfer reaction. Instead, we propose a composite mechanism which can account for all our experimental data, whether kinetic, stoichiometric, or spectral.

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