

Kinetics Evidence for a Complex between Peroxynitrous Acid and Titanium(IV)

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The reaction between TiO_2^{2+} and ONOOH in 0.9 M H_2SO_4 provides evidence for direct formation, previously unobserved, of a HOONO –metal complex. The reaction proceeds via formation of an end-on complex ($k = 3.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$) that rearranges to form a side-on complex ($k \approx 20 \text{ s}^{-1}$). With ONOOH in excess, this rearrangement proceeds more slowly ($k \approx 0.1 \text{ s}^{-1}$), probably because multiple hydrogen oxoperoxonitrate molecules form end-on complexes with oxotitanium(IV) and hinder rearrangement to the side-on complex. The absorption spectrum of the final product is that of TiO_2^{2+} . Presumably, during the rearrangement or later, NO^+ is lost.

Since 1895 it has been known that addition of ammonium fluoride and ammonia to an acidic solution of titanium and hydrogen peroxide¹ yields a crystalline complex with a peroxide group bound to the titanium. Schwarz and Giese² argued that in all likelihood the peroxide group was bound side-on and that, by implication, the coordination number of titanium(IV) was seven. This suggestion was shown to be correct in the 1970s when Schwarzenbach published the structures of side-on coordinated hydrogen peroxide Ti(IV) complexes.^{3–5} A side-on *tert*-butylhydroperoxide–titanium(IV)⁶ complex has also been reported, as well as two alkylhydroperoxide–vanadium(V)⁷ complexes. We are interested in the stabilization of oxoperoxonitrate(1–) by complexation with transition metals and speculated that hydrogen oxoperoxonitrate could form a complex with titanium(IV) similar to that with hydrogen peroxide.

A few oxoperoxonitrate–metal complexes have been observed, but these were always synthesized from a superoxo–metal complex and nitrogen monoxide. For instance, Herold and co-workers have shown that nitrogen monoxide reacts with oxymyoglobin to form a oxoperoxonitrate–iron(III) intermediate.^{8,9} We subsequently demonstrated that the reaction of pentacyanosuperoxocobaltate(III) with nitrogen monoxide yields an oxoperoxonitrate complex¹⁰ that is surprisingly stable at neutral pH and slowly isomerizes at acidic pH.¹¹ Similarly synthesized transient chromium(III)– and rhodium–oxoperoxonitrate complexes have been described by Bakac and co-workers.^{12,13} However, direct formation of an oxoperoxonitrate–metal complex from a reaction of oxoperoxonitrate(1–) or its protonated form with a metal ion has not yet been reported.

Potassium oxoperoxonitrate was synthesized from solid potassium superoxide and nitrogen monoxide and freed from hydrogen peroxide as described previously.¹⁴ The oxotitanium solution was prepared by dissolving freshly synthesized oxotitanium sulfate in 0.9 M sulfuric acid. Precipitated titanium dioxide was removed by filtration. The kinetics of the reaction of oxotitanium(IV) with hydrogen oxoperoxonitrate were followed with an Applied Photophysics SX17MV single-wavelength stopped-flow spectrophotometer at 25 °C. Kinetics observations were made with detection between 400 and 560 nm. Some of the kinetics parameters were obtained with the SPECFIT/32 program (Binstead R.; Zuberbühler, A. D. *SPECFIT/32*; Spectrum Software Associates: Chapel Hill, NC, 2000–2002).¹⁵

When hydrogen oxoperoxonitrate (0.25 mM) is mixed with oxotitanium(IV) in excess under pseudo-first-order conditions

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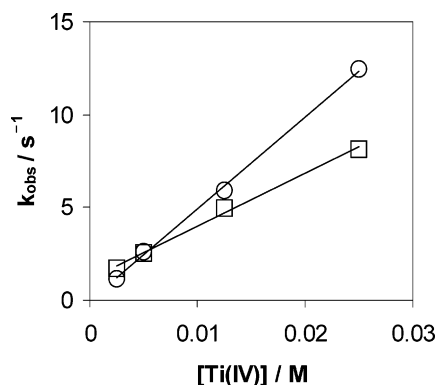


Figure 1. Rates of reaction of 0.25 mM H₂O₂ (○) and ONOOH (□) with excess oxotitanium(IV) in 0.9 M H₂SO₄ at 25 °C. The rates are based on measurements at 410 nm. Bimolecular rate constants of $(2.8 \pm 0.1) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ and $(4.9 \pm 0.1) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ for the reactions of TiO²⁺ with ONOOH and H₂O₂, respectively, are calculated from these data. The errors are smaller than the symbols.

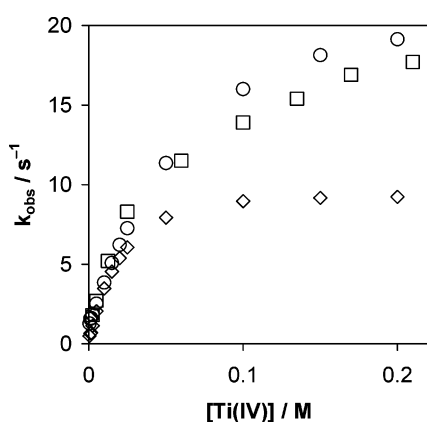


Figure 2. Saturation observed when ONOOH is mixed at higher TiO²⁺ concentrations: experimental results (□); results of the two-step model simulation (○); results of the dissociation model (◇).¹⁴ The concentration of ONOOH was 0.25 mM. The conditions were as described in the caption of Figure 1.

in 0.9 M sulfuric acid, an increase in absorption at 410 nm is observed. The reaction is first-order in oxotitanium(IV), as shown in Figure 1. From the slope of the lower line, a rate constant of $3.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ is derived. For comparison, oxotitanium(IV) was mixed with hydrogen peroxide under identical conditions, see Figure 1, upper line. As expected, the extrapolation of this line passes through the origin, and a bimolecular rate constant of $4.9 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ is found, in excellent agreement with the literature.¹⁶ When the oxotitanium(IV) concentration is further increased in the reaction with hydrogen oxoperoxonitrate, one observes saturation, see Figure 2. This behavior can be modeled with two sequential reactions, the fast bimolecular formation of a colorless end-on complex, reaction 1, followed by the intramolecular rearrangement to a yellow side-on complex, reaction 2. At low oxotitanium(IV) concentrations, the association is rate-limiting, at higher concentrations, the intramolecular rearrangement. The rate constant of reaction 2 is estimated to be near 20 s^{-1} . In Figure 1, an intercept of 0.71 s^{-1} is obtained by the extrapolation of the hydrogen

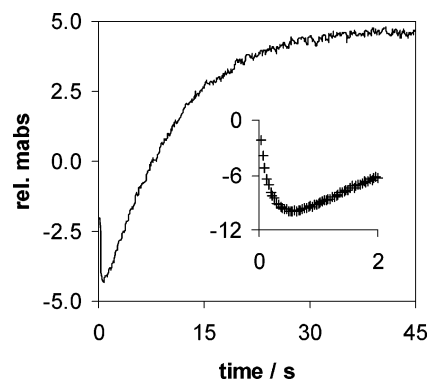
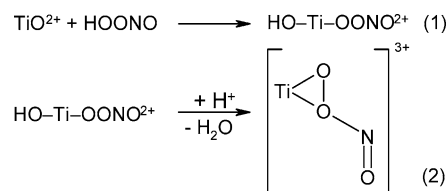


Figure 3. With ONOOH present in excess, there is, after an initial decrease in absorption due to the isomerization reaction and complexation, a much slower increase in absorption than as shown in Figure 2. Rel. mabs is relative milliabsorbance.

oxoperoxonitrate data. This is reproduced by a numerical simulation of the reaction model, which yields a value of 1.3 s^{-1} . Given the presence of oxotitanium(IV) in excess, this rate constant reflects the dissociation of hydrogen oxoperoxonitrate from the end-on titanium complex, rather than the isomerization to nitrate. Except at very small titanium concentrations, the traces did not follow pseudo-first-order kinetics. Better fits were obtained with the sum of two exponential terms. The high oxotitanium(IV) concentration data in Figure 2 were obtained by fitting the late parts of the traces. The validity of the two-step model is further confirmed by the simulated values for high oxotitanium(IV) concentrations (Figure 2). The simulation data represented by circles (○) fit the experimental results (□) quite well. For comparison, an alternative model which assumes that hydrogen oxoperoxonitrate is in equilibrium with hydrogen peroxide and nitrous acid, as proposed by Merényi et al.,¹⁴ followed by the well-known complexation of the hydrogen peroxide, was also simulated. It is shown in Figure 2 (◇) that the forward rate constant for the hydrogen oxoperoxonitrate equilibrium suggested by Merényi et al., about 6 s^{-1} for 0.9 M acid,¹⁷ is not in agreement with the complexation rate observed at high oxotitanium(IV) concentrations.



With hydrogen oxoperoxonitrate in excess, one observes at 410 nm a fast decrease first, and then an increase in absorption with a rate constant of $0.08\text{--}0.16 \text{ s}^{-1}$ (Figure 3). The initial decrease is due to the decreasing hydrogen oxoperoxonitrate concentration caused by isomerization and complexation, while the increase arises from the formation of the side-on titanium-peroxo complex from the initial end-on species. The increase continues for 30–40 s, though after

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2 s all free hydrogen oxoperoxonitrate would have disappeared by isomerization.

Rate constants between 0.08 and 0.16 s⁻¹ are derived from traces such as the one shown in Figure 3. The rearrangement is much slower when hydrogen oxoperoxonitrate is present in excess, ~0.1 vs 20 s⁻¹. We assume that multiple hydrogen oxoperoxonitrate molecules form end-on complexes with oxotitanium(IV), and that they mutually hinder the rearrangement to the side-on complex. The final absorption band is qualitatively identical to the one formed from the reaction between oxotitanium(IV) and hydrogen peroxide, with a maximum at 410 nm. However, the yield is at best 40%, even with a concentration of hydrogen oxoperoxonitrate 100 times higher than that of oxotitanium(IV). Either 60% of the initial end-on complex decays to nitrate within the coordination sphere or after dissociation, and 40% to nitrite and peroxide, or a side-on complex is formed with an extinction coefficient of 40% of the peroxo complex. We favor the latter possibility, because the transition from end-on to side-on is expected to be hindered when multiple hydrogen oxoperoxonitrate molecules are bound, while the dissociation to nitrosyl and hydrogen peroxide under such conditions is not, or is less so. The extinction coefficient of the side-on oxoperoxonitrate complex may be smaller than that of the peroxo complex because the nitrosyl moiety competes with the titanium in charge transfer. However, both mechanisms may be operating. The formation of nitrite would be analogous to that observed with a macrocyclic rhodium(III) oxoperoxonitrate(1-) complex.¹²

The side-on complex is not infinitely stable: the structure of the complex obtained after a nitrilotriacetate complex of oxotitanium(IV) is mixed with hydrogen oxoperoxonitrate shows that there is a side-on O₂²⁻, not an ONOO⁻ (Wick, P. K.; Kissner, R.; Koppenol, W. H. Unpublished, 2000). It would seem, therefore, that the nitrosyl cation dissociated from the complex during or after the rearrangement from end-on to side-on. However, it is possible, and even likely, that the nitrosyl cation was removed during the recrystallization

from hot water, which was necessary to obtain crystals for X-ray analysis. If the nitrosyl cation dissociates from the (oxoperoxonitrate)titanium(IV) complex, then nitrite should be found as a final product. However, nitrite could not be determined because we found that the peroxotitanium complex oxidizes it to nitrate ($k = 7.9 \text{ M}^{-1}\text{s}^{-1}$), and nitrite is also a contaminant in most oxoperoxonitrate(1-) syntheses. For these reasons, nitrite was removed, and only nitrate was determined by anion chromatography with conductometric detection, as described before.¹⁸ After the reaction of hydrogen oxoperoxonitrate with excess oxotitanium(IV) was finished, nitrite was removed with sulfamidic acid, $k = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.¹⁹ The high concentration of sulfuric acid normally used during this reaction, 0.9 M, would lead to sulfate concentrations that interfere with the chromatographic analysis. Therefore, the reaction of oxotitanium(IV) with hydrogen oxoperoxonitrate was carried out in 0.18 M sulfuric acid. The acid was neutralized with potassium hydroxide, and barium tetraoxochlorate was added. The precipitated barium sulfate was washed with water and removed by centrifugation; the water was added to the supernatant. Concentrations of 30% and 60% nitrate, relative to hydrogen oxoperoxonitrate, were found. These results are compatible with partial loss of the nitrosyl cation from coordinated ($\kappa O'$ or $\kappa O, \kappa O'$) oxoperoxonitrate(1-), and do not support exclusive isomerization of the bound oxoperoxonitrate(1-) to nitrate inside the metal complex, as we observed for the pentacyano(oxoperoxonitrate)cobaltate(III) complex.¹¹

We conclude that hydrogen oxoperoxonitrate directly forms a complex with oxotitanium(IV).

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