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Ozone from Iron(III) Porphyrin, Nitrite Ion, and Oxygen

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Ozone is well known as an extremely powerful oxidant. Its decomposition to oxygen proceeds with the release of 143 kJ/mol, and it reacts with a broad range of inorganic and organic structural types.[1,2] It is formed in the atmosphere by the photolysis of O_2 and NO_2. The resulting oxygen atoms combine with O_2 to produce O_3. The combination of certain peroxy radicals may also result in O_3.[3] In addition to photolysis, ozone can be synthesized from dioxygen by electrolysis, electrical discharge, ionizing radiation, and UHF fields. The actual chemistry of these processes is complex and not fully understood.[2,3] In contrast, the chemical generation of ozone is rare. However, small quantities have been reported to occur upon the addition of hydrogen peroxide to selenic acid,[4] the decomposition of potassium peroxydisulfate by acid,[5] the reaction of fluorine with aqueous KOH,[6] and the oxidation of thin films of aluminum.[7] Presumably oxygen atoms are generated to some extent in these reactions.

The oxidations of iodide to iodine[2] and nitrite to nitrate[8] are common tests for the presence of ozone in trace quantities. However, the most characteristic reaction of ozone is its reaction with olefins.[2] The sequence ozonolysis followed by reduction of the ozonides with zinc in acetic acid, to aldehydes and ketones, is the classic method for locating the position of double bonds in unknown structures.[9] This procedure has been supplanted by modern NMR analyses, but it represents an excellent means of establishing the transient presence of ozone in a reaction mixture.

We have recently reported a series of facile oxygen atom transfers from iron(III) porphyrin NO_2^- adducts to a broad range of substrates under argon[10] (eq 1, S = substrate). Typical reactions entail oxygen insertion into carbon−hydrogen bonds,

$$\mathrm{PFe^{III}} + \mathrm{NO_2}^- \rightleftharpoons \mathrm{PFeNO_2} \xrightarrow{\mathrm{S}} \mathrm{PFe^{II}NO} + \mathrm{SO} \qquad (1)$$

olefin epoxidation, and oxygen atom transfers to sulfides, phosphines, carbon monoxide, and nitric oxide. The driving force for these reactions resides in the enormous thermodynamic stability of the porphyrin iron(II)−NO adducts.[11] In this work we address the question: Can dioxygen be a substrate in these reactions?

As a consequence of related studies of the reactions of oxygen−heme protein adducts with simple N−O bonded species, it became clear that the character of the reactions in air and under argon was markedly different. Thus, the autocatalytic reaction of oxymyoglobin with NO_2^- in air requires intermediates that are not apparent under argon.[12] This led to the speculation that ozone may be an entity driving the autocatalysis. Perhaps like CO and NO, oxygen could be a substrate in reaction 1?

To test this unlikely hypothesis, octaethylporphyrin iron(III) chloride and potassium crown ether (18-crown-6) nitrite were reacted in an oxygen atmosphere with three substances that have been established to be inert under argon. That is, they are not substrates in reaction 1. These ozone scavengers are nitrite ion and the two olefins 2,3-dimethyl-2-butene and 2-methyl-2-butene. Reaction conditions were the same as those described previously[10] except that they were carried our under oxygen.

In the first reaction, an excess of NO_2^- (5.2×10^{-5} mol of K^+ (18-crown-6) NO_2^-) was allowed to react with ClFe(III)-OEP (2×10^{-5} mol) in 4 mL of *N*-methylpyrrolidone (NMP) − 1% acetic acid. The thoroughly oxygen-purged, sealed, stirred reaction was concentrated to dryness in vacuo after 16 h. The recovery of combined nitrite and nitrate from an aqueous extract was 73%.[13] The ratio of NO_3^- to NO_2^- was 0.5 ± .1 (theoretical, 0.6). The generation of NO_3^- was confirmed by IR analysis of a portion of the concentrated aqueous extract. Strong bands corresponding to nitrate (1350 cm^{-1}) and nitrite (1275 cm^{-1}) were observed.[14a]

With the olefin traps, a large excess of the olefin was employed to compete with the potential NO_2^- reaction with ozone. Two mL of NMP−1% HOAc and two mL of olefin containing 2×10^{-5} mol of ClFe(III)OEP and 2.6×10^{-5} mol of K(18-crown-6)$^+$ NO_2^- were stirred in an oxygen atmosphere for 16 h. The reaction mixture was briefly purged with argon and reduced with zinc dust (0.2−0.4 g) and acetic acid (additional 0.5 mL) for 3 h. The low-temperature (bp < 60 °C) reaction distillate was analyzed by gas chromatography (GC), infrared, and GC−mass spectroscopy. With 2,3-dimethyl-2-butene, the yield of acetone[15] was 100 ± 10% calculated on the basis of 2 mol of acetone per mol of PFe^{III} charged. The reaction distillate exhibited a strong carbonyl absorption at 1722 cm^{-1} corresponding exactly to that of acetone in tetramethylethylene.

With 2-methyl-2-butene, the yield of acetone following the reaction and reduction with Zn/HOAc and distillation was 90%, but the acetaldehyde recovery (GC) was lower (50%).[16] Both acetone and acetaldehyde from these reactions were confirmed by GC−MS.[17]

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[13] (a) Chow, T. J.; Johnstone, M. S. *Anal. Chem. Acta* **1962**, *27*, 441. (b) A possible additional source of nitrate in this milieu, following reaction 2, would be the reaction of PFeNO with O_2 (cf. ref 12).

[14] (a) The same reaction under argon yielded no NO_3^-. Similarly a reaction under oxygen, but without porphyrin, produced no nitrate. (b) All control reactions were run and worked up in a manner identical to that described in the text and consisted of runs (i) with substrate and oxygen, but no porphyrin; (ii) porphyrin, oxygen, and substrate, but no nitrite; (iii) porphyrin, nitrite, and substrate, but no oxygen (reactions under argon). No reaction occurred under any of these conditions. In all cases, only nitrite salt and unreacted olefin were recovered. In particular, neither nitrate, acetone, or acetaldehyde was detected in any control run.

[15] A 2 ft × 1/8 in. Porapak P column at 85 °C/30 mL/min He was employed. Acetone and (2.0 min) tetramethylethylene (2.8−6 min were the only peaks present and corresponded exactly to an authentic standard.

[16] A 5 ft × 1/8 in. Porapak T column at 125 °C/40 mL/min He was employed: acetaldehyde (4 min), trimethylethylene (9−12 min), acetone (15 min). Consistent injection of acetaldehyde was difficult. Estimation of the combined yield of acetone and acetaldehyde via IR of the distillate (1718−1720 cm^{-1}) and comparison with a standard were 90 ± 10%.

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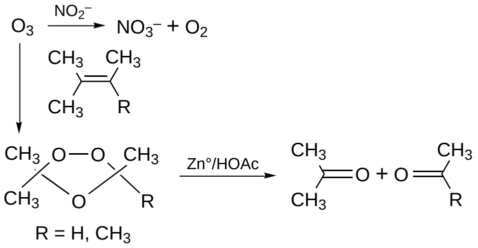
A summary of these results is given by eqs 2 and 3. Reaction 2 is presumed to be reversible since ozone is known to rapidly react with NO in the gas phase.[18]

$$\mathrm{PFeNO_2} + \mathrm{O_2} \rightleftharpoons \mathrm{PFeNO} + \mathrm{O_3} \qquad (2)$$



(3)

The subsequent reactions with nitrite and the olefins establish that ozone is indeed a product that can be trapped in these reactions under oxygen. It should be emphasized that a series of control runs[14b] from which each of the reactants was selectively eliminated established that the iron porphyrin, oxygen, and nitrite salt are all essential for the olefin oxidations to occur.

These results may explain the instability of TPPFe^{III} nitrite adducts originally reported by Scheidt and colleagues[19] that we did not observe under argon. Moreover, in addition to explaining, perhaps, the century old[20] riddle of the autocatalytic oxidation of oxyhemoglobin and oxymyoglobin by nitrite ion, they may also be relevant to other biochemical processes that involve heme−oxygen adducts and nitrite ion. As one example, NO synthetase is, in part, a P-450 like protein,[21] and in aqueous solution NO is established[22] to be oxidized by oxygen to NO_2^-. Thus, tissue damage by ozone generated in vivo is a possibility.

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(17) For acetone, GC-MS analysis showed P (58) and P−CH_3 (43); for acetaldehyde P (44), P−H (43), and P−CHO (15) were observed.

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