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Formation of Peroxynitrite by Sonication of Aerated Water

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The formation of nitrate and nitrite anions upon sonication of aerated water is well-known.[1,2] The implosion of the cavitational bubble generates temperatures that are sufficient to dissociate a diatomic operating gas, as well as the water vapor contained in it to $^{\bullet}$OH and H$^{\bullet}$ (cf. refs 3−6). The processes involving the sonolytic generation of nitric oxide, the initial precursor of the nitrogenous anions, and a variety of subsequent reactions have been extensively discussed.[7] The reaction-kinetic situation is complicated by the fact that the reaction temperature varies enormously in space and time across the cavitational event which is, moreover, a two-phase system. Briefly put in the present context, the initial steps taking place within the cavitational bubble include reactions 1−3 [1 and 2 endothermic] where the displacement reaction 2[8] unlocks the dinitrogen molecule, making nitrogen available for the subsequent reactions.

$$O_2 \rightarrow 2\,O \qquad (1)$$

$$N_2 + O \rightarrow NO^{\bullet} + N^{\bullet} \qquad (2)$$

$$N^{\bullet} + M \rightarrow\rightarrow \text{products} \qquad (3)$$

M stands for any component of the system which is reactive toward nitrogen atoms. Straightforward routes to nitrate and nitrite are supposed to follow reactions 4−6 and/or reactions 7−9.

$$NO^{\bullet} + O_2 \rightleftharpoons ONOO^{\bullet} \qquad (4)$$

$$ONOO^{\bullet} + NO^{\bullet} \rightarrow 2\,^{\bullet}NO_2 \qquad (5)$$

$$2\,^{\bullet}NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \qquad (6)$$

$$NO^{\bullet} + {}^{\bullet}NO_2 \rightarrow 2\,HNO_2 \qquad (7)$$

$$NO^{\bullet} + {}^{\bullet}OH \rightarrow HNO_2 \qquad (8)$$

$$^{\bullet}NO_2 + {}^{\bullet}OH \rightarrow HNO_3 \qquad (9)$$

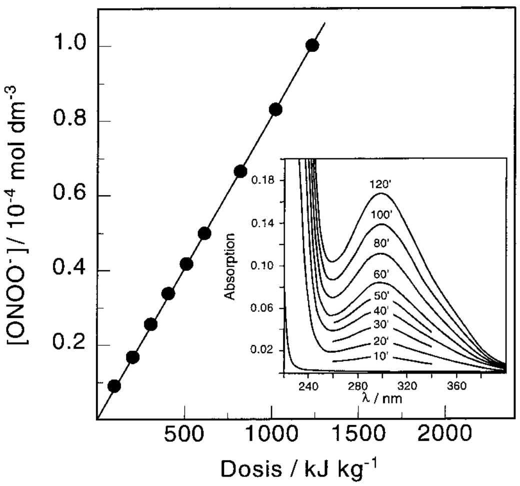

Figure 1. Linear dose-dependence of peroxynitrite formation in aerated water (pH 12) upon sonication. Frequency, 321 kHz; dose rate 170 W kg^{-1} as measured by calorimetry.[9] Inset: Optical absorption spectrum of aerated water (pH 12) after various sonication times. The absorption band near 300 nm is due to peroxynitrite.

Of these, the recombination of $^{\bullet}$OH with $^{\bullet}$NO and $^{\bullet}$NO$_2$ will take place mostly near the bubble-liquid interface as it has been shown that for the most part the OH radicals do not penetrate into the bulk of the aqueous phase.[9−11]

Frequently, aqueous-solution sonolysis experiments have been carried out under conditions where the starting pH is near neutral but otherwise unspecified since in the case discussed here, as well as in the case of other substrates that form acidic products upon sonolytic oxidation, the pH drifts off into the acidic range in the absence of a buffer. We have now carried out the sonolysis of air-saturated aqueous NaOH (pH 12) and have observed the production of peroxynitrite. The dose-dependence of the formation of this product is shown in Figure 1.

The product has been unambiguously identified on the basis of its optical absorption spectrum[12] (inset in Figure 1). In contrast to its anion, peroxynitrous acid (pK_a = 6.5−6.8) is quite unstable (k_{10} in the order of 1 s^{-1}) and decomposes into nitric acid largely via a free-radical pathway [reactions 10, 11, 9] (cf. refs 13−16), that is, this compound cannot be observed in nonalkaline solutions by conventional methods.

$$ONOO^- + H^+ \rightleftharpoons ONOOH \qquad (10)$$

$$ONOOH \rightleftharpoons {}^{\bullet}NO_2 + {}^{\bullet}OH \qquad (11)$$

Peroxynitrous acid is in fact also produced alongside nitric acid when the radicals $^{\bullet}$OH and $^{\bullet}$NO$_2$ recombine [reaction −11]. In the bulk aqueous phase, the ratio k_9/k_{-11} is reported to be about unity,[16] while in the gas phase it is more in favor of nitric acid (k_9/k_{-11} in the order of 10).[17] Moreover, it seems likely that the

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concentration of $^{\bullet}NO_2$ in the vicinity of the cavitational bubble is relatively small: its formation via reactions 4 and 5 is two-step, going through the nitric oxide peroxyl radical intermediate whose concentration is small because of the efficient back-reaction −4[18] [reaction −4 has in fact been implicated in the formation of nitric oxide in the photolysis of aqueous nitrate solutions[19]]. There may however be a contribution to the formation of $^{\bullet}NO_2$ in the vicinity of the cavitational bubble via reaction 8, followed by reaction 12.

$$^{\bullet}OH + HNO_2\,(NO_2^-) \rightarrow {}^{\bullet}NO_2 + H_2O\,(OH^-) \quad (12)$$

We think that the likely pathway to peroxynitrite in the present sonolytic system is via reactions 13−16. It is known that in the absence of other OH-radical scavengers the concentration of H_2O_2 in the interfacial layer can approach 10^{-2} M.[9−11,20] In this location, it is exposed to further OH-radical attack, giving rise to the formation of superoxide which is known to recombine with nitric oxide.[14,21,22]

$$2\,^{\bullet}OH \rightarrow H_2O_2 \quad (13)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (14)$$

$$HO_2^{\bullet} \rightleftharpoons O_2^{\bullet -} + H^+ \quad (15)$$

$$O_2^{\bullet -} + NO^{\bullet} \rightleftharpoons ONOO^- \quad (16)$$

The results shown in Figure 1 imply an energy-specific yield, called *G* value, of 0.8×10^{-10} mol $J^{-1}$of sonic energy absorbed.[23] In *argon*-saturated water, one observes a *G* value near 7.5×10^{-10} mol J^{-1} for the formation of H_2O_2, and a *G* value of 16×10^{-10} mol J^{-1} for the OH radical emerging from the interior of the cavitational bubble and entering the interfacial layer.[9,10] There are indications that with *air* as the operating gas the situation regarding the H_2O_2 and OH-radical *G* values is different, but not widely so.[24]

Hydrogen peroxide and peroxynitrite, “molecular oxidants” in contrast to the free-radical, transient oxidants such as $^{\bullet}OH$ and $^{\bullet}NO_2$, become homogeneously dispersed throughout the bulk of the solution. The implication is that a solute that is sensitive to the strong oxidant peroxynitrite/peroxynitrous acid[25,26] may under these conditions undergo sonolytic transformation not only “directly” near the cavitational bubble but in part in the bulk *mediated* by peroxynitrite.

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