ISSN 0018-1439, High Energy Chemistry, 2016, Vol. 50, No. 5, pp. 424–425. © Pleiades Publishing, Ltd., 2016.
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SHORT COMMUNICATIONS
PLASMA CHEMISTRY

Spark Plasma Radiation-Induced Formation of Long-Lived Active Species

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Received January 23, 2016

DOI: 10.1134/S001814391605012X

Peroxynitrite and peroxynitrous acid is the active form of nitrogen. The main channels of the formation and decay of peroxynitrite and peroxynitrous acid are surveyed in [1]. The formation of these products in water by the action of plasma radiation of spark discharge in air was detected in [2] by measuring UV spectra for peroxynitrite and in [3] by the reduction of stable free radical $DPPH^{\cdot}$ to identify peroxynitrous acid. Both products appear 3 to 4 days after plasma radiation treatment, reaching a maximum yield by the 7th or 8th day after the treatment and disappear on the 14th day. Their instantaneous concentration of about 10^{-5} mol $L^{-1}s^{-1}$. The appearance of these products was associated with the formation and decay of a long-lived complex (..ONOOH ... $ONOO^{-}$..) [4]. Skepticism was caused by the fact that the decay products of this complex could not be seen for the first 3 to 4 days. The aim of this work was to study the mechanism of the reactions of the active species produced by the decay of the long-lived complex, as well as the feasibility of detection of the decay products of the complex.

A 45-mL sample of doubly distilled water (pH_0 6.3) was treated in a fluoroplastic Petri dish with spark plasma radiation for 30 min. An IR-10 radiation source was used [4]. Immediately after treatment, the pH was 2.8. Nitric and nitrous acids were identified in the products using UV spectra and ion-selective electrodes [4]. The nitrous acid concentration was 0.005 mol/L [4].

In this study, the active species were determined iodometrically. To the 45-mL sample of water, 4 mL of 5% KI solution and 4 mL of dilute sulfuric acid (1 : 4) were added. The amount of released iodine was determined by titration with 0.02 N sodium thiosulfate. To experimentally evaluate the possibility of oxidation of I^{-} with nitric acid, the same reagents were added to the nitric acid solution with pH 2.5–2.8. No change in color of the solution within 5 min was observed. Oxidation of I^{-} could occur with nitrous acid and peroxynitrite/peroxynitrous acid. Water samples of a 45 mL volume treated for 30 min each were accumulated and placed in separate containers. These samples were stored for a period of 1 to 14 days, after which the presence of active species in the sample was determined iodometrically. Measurements were made on four to five samples for each holding time. The results of titration of water samples immediately after treatment and after holding for 1 to 14 days are shown in the figure (curve *1*).

To assess the oxidation of I^{-} with nitrous acid alone, a $NaNO_2$ solution with a concentration of 0.005 mol/L (equal to the concentration of nitrous acid in the sample immediately after treatment) was prepared. Concentrated nitric acid was added to the $NaNO_2$ solution and the pH was brought to 2.8. Nitrous acid oxidizes I^{-} according to the reaction:

$$2I^{-} + 4H^{+} + 2NO_2^{-} \rightarrow I_2 \downarrow + 2NO \uparrow + 2H_2O. \quad (1)$$

Nitrous acid (pK_a 3.4) is weakly dissociated at pH 2.8, but reaction (1) goes to completion; as NO_2^{-} ions are consumed, HNO_2 molecules dissociate. This process is slow; therefore, the samples were held for 5 min before titration. In an acidic medium, $ONOOH/ONOO^{-}$ exists mainly in the form of peroxynitrous acid, pK_a ($ONOOH/ONOO^{-}$) = 6.8. Peroxynitrous acid also oxidizes I^{-}:

$$2ONOOH + 2I^{-} \rightarrow I_2 \downarrow + 2NO \uparrow + H_2O. \quad (2)$$

The results of titration of the $NaNO_2 + HNO_3$ solution immediately after preparation and within 14 days of storage are also shown in the figure (curve *2*). In an acidic medium, NO_2^{-} ions slowly decompose to release NO and form nitric acid. Therefore, the consumption of 0.02 N thiosulfate for titration of the acidic $NaNO_2$ solution decreases over time from 14 mL to 0.1 mL after 14 days.

If plasma radiation induces the formation of the complex, which decays into $ONOOH/ONOO^{-}$, the degradation products of the complex will interact withNO_2^{-} ions [5]:

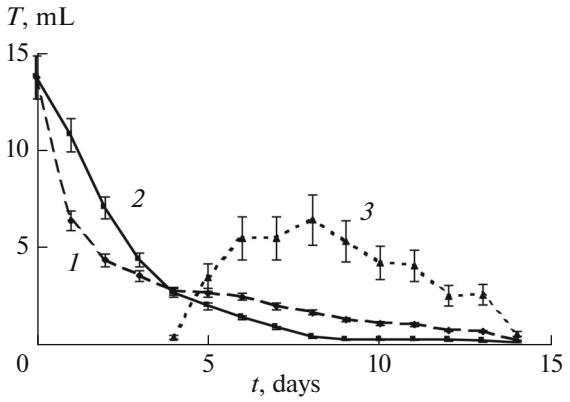

Fig. 1. Consumption of 0.02 N sodium thiosulfate (T, mL) for titration of a 45-mL water sample *t* days after preparation: (*1*) water treated with plasma radiation for 30 min; (*2*) $NaNO_2 + HNO_3$ solution, pH 2.8; and (3) difference (T1 – T2) × 5.

$$ONOOH + NO_2^- \leftrightarrow adduct^- \rightarrow NO_2^- + NO_3^- + H^+. \quad (3)$$

The rate of reaction (3) is highly dependent on the reactant concentration. The observed rate constant is $k_{3obs} = 1.1–6\ s^{-1}$ [5]. Both peroxynitrous acid and NO_2^- ions are consumed in reaction (3).

The consumption of thiosulfate for titration $NaNO_2 + HNO_3$ solution decreases with holding time only as a result of degradation of NO_2^- ions. In the water sample treated with plasma radiation at the same initial concentration of NO_2^- ions, the decrease in thiosulfate consumption for titration is due to both decomposition of the NO_2^- ions in the acidic medium and the involvement of the ions in reaction (3). Therefore, the consumption of thiosulfate for titration during the first three days decreases faster in the sample of treated water than in $NaNO_2 + HNO_3$ solution.

When the concentration of NO_2^- ions on the 4th day after the treatment decreases, the consumption of peroxynitrous acid in reaction (3) also decreases. In this case, the role of reaction (2) in the oxidation I^- increases, and the contribution of peroxynitrous acid in the formation of I_2 becomes predominant. Over the first three days, almost all peroxynitrous acid can be consumed in reaction (3), and it is for this reason that neither peroxynitrite nor peroxynitrous acid was found during the first three days [2, 3]. They become detectable by the 3rd to 4th day after treatment. Their yield reaches a maximum 7–9 days after treatment, when NO_2^- ions almost completely decompose. The titer difference T1 – T2 (curve *3*) becomes greater than zero on the fourth day and reaches a maximum at 7–9 days.

Thus, with peroxynitrite and peroxynitrous acid are consumed in reaction (3) with NO_2^- ions during first three days after the treatment. They become noticeable after the decomposition of the NO_2^- ions and completely disappear on the 14th day when the complex decomposes. The concentration of the complex, which can be determined on the basis of the titration data is $(2.5 \pm 0.5) \times 10^{-3}$ mol/L. This value is consistent with the results obtained in [3]: $(1.8 \pm 0.4) \times 10^{-3}$ mol/L.

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Translated by S. Zatonsky