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Effect of dissolved oxygen on the radiolytic conversion of nitrate ions in aqueous solutions in the presence of formate

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A dose higher than 2 kGy and a tenfold excess of formate over nitrate are required for the almost complete degradation of ~10^{-4} mol dm^{-3} nitrate in an aerated aqueous solution.

The radiolytic decomposition of environmental pollutants in aqueous solutions is a promising method for wastewater treatment.[1] Nitrates and formates frequently occur in industrial wastewater. Formate in aqueous solutions is characterised by a low radiolytic stability. Under electron-beam irradiation, it is irreversibly decomposed to CO_2 and H_2O.[2,3] Nitrate is resistant to irradiation. The noticeable effect of irradiation on nitrate in aqueous solutions is observed only in the presence of effective scavengers of OH radicals.[4,5] Earlier,[5] we found that the presence of nitrate and formate in a deaerated aqueous solution can provide deep decomposition of nitrate. In the absence of oxygen, formate actively traps OH radicals and slowly reacts with the reduction products of water radiolysis,[5,6] the hydrated electron e^-_{aq} and the H atom. These properties of formate are responsible for the selective reduction of nitrate in a deaerated solution under irradiation

$$NO_3^- \xrightarrow{e^-_{aq},\ H} NO_2^{:} \xrightarrow{e^-_{aq},\ H} NO_2^- \xrightarrow{e^-_{aq},\ H} NO \xrightarrow{e^-_{aq},\ H} N_2O \xrightarrow{e^-_{aq},\ H} N_2 \quad (1)$$

and minimise the effect of back oxidation processes

$$NO \xrightarrow{^{\cdot}OH} NO_2^- \xrightarrow{^{\cdot}OH} NO_2^{:} \xrightarrow{^{\cdot}OH} NO_3^-. \quad (2)$$

In actual practice, the removal of oxygen from wastewater (deaeration) is labour intensive. Nitrate decomposition without deaeration is preferable. In this work, the radiolytic reduction of nitrate in aerated diluted solutions with formate additive is considered.

The model solutions were prepared in distilled water using $NaNO_3$ and HCOOLi of extra pure grade. A Specord M40 spectrophotometer was used for optical measurements. The analysis for nitrogen compounds was performed by standard procedures.[7,8] Oxalic acid (oxalate) was determined using the copper–benzidine complex.[9,10] A U-12F linear accelerator was used as a source of electron radiation (electron energy of 5 MeV, pulse duration of 2.3 μs, pulse repetition frequency of 400 Hz and dose rate of 10 Gy s^{-1}). The solutions were deaerated for 45 min by bubbling argon and irradiated in glass ampoules with ground-glass stoppers. The solution volume was 10 ml and the headspace volume was 5 ml.

The main intermediate in the radiolytic transformations of formate in aqueous solutions is the CO_2^- radical anion.[1–3] The latter is formed because formate captures either an OH radical (predominantly)

$$^{\cdot}OH + HCOO^- \longrightarrow H_2O + CO_2^- \quad (k = 3.1\times10^9\ dm^3\ mol^{-1}\ s^{-1}) \quad (3)$$

or an H atom:

$$^{\cdot}H + HCOO^- \longrightarrow H_2 + CO_2^- \quad (k = 3.0\times10^8\ dm^3\ mol^{-1}\ s^{-1}). \quad (4)$$

As a rule, the CO_2^- radical anion displays reduction properties. The predominant reaction of formate in an irradiated aqueous solution is dimerisation[6] with formation of oxalate:

$$2CO_2^- \longrightarrow C_2O_4^- \quad (2k = 1.5\times10^9\ dm^3\ mol^{-1}\ s^{-1}). \quad (5)$$

The radiation-chemical yield[5] of oxalate in deaerated aqueous solutions (1×10^{-3}–2×10^{-3} mol dm^{-3} formate) at a dose of 2 kGy was 0.153 μmol J^{-1}. Figure 1 (curve *1*) indicates that, under the same conditions, the maximum yield of oxalate in an aerated solution is 0.128 μmol J^{-1}. Thus, oxalate was almost not formed at initial formate concentrations lower than 5×10^{-4} mol dm^{-3}. Such an induction period in the aerated solution results from the capture of the CO_2^- radical anion by dissolved oxygen[1,6]

$$2CO_2^- + O_2 \longrightarrow CO_2 + O_2^- \quad (k = 3.0\times10^9\ dm^3\ mol^{-1}\ s^{-1}) \quad (6)$$

and, as a consequence, reaction (5) is depressed.

In addition to reaction (6) in the irradiated aqueous solution, oxygen actively decays in reactions with the primary products of water radiolysis,[1,6] giving rise to formation of additional oxidative species:

$$O_2 + e^-_{aq} \longrightarrow O_2^- \quad (k = 1.9\times10^{10}\ dm^3\ mol^{-1}\ s^{-1}) \quad (7)$$

$$O_2 + H \longrightarrow HO_2 \quad (k = 2.0\times10^{10}\ dm^3\ mol^{-1}\ s^{-1}) \quad (8)$$

$$O_2^- + H^+ \rightleftharpoons HO_2 \quad (pK_a = 4.7) \quad (9)$$

However, at a high dose rate, the rate of buildup of radiolytic products in the bulk of solution is much higher than the rate of oxygen diffusion into the solution from air. Thus, during irradiation, oxygen is irreversibly consumed in fast reactions with radiolytic products and the role of reactions (6)–(9) is gradually depressed. At doses higher than 0.5 kGy, the further radiolytic processes become similar to processes in deaerated solutions; however, the quantitative parameters of nitrate degradation are changed because of the reactions of accumulated products with oxygen.

In the presence of 1×10^{-4} mol dm^{-3} nitrate, the dynamics of radiolytic oxalate accumulation was changed. The detectable accumulation of oxalate was observed only at a formate concentration above 8×10^{-4} mol dm^{-3}. The maximal yield of oxalate in the presence of nitrate at doses of 3–7 kGy is 0.08 μmol J^{-1}. Such a decrease in the oxalate yield can be caused by depressing reaction (3) because a part of OH radicals is involved in back oxydation (2). The decrease in the yield of CO_2^- radical anions results in the depression of dimerisation (5), *i.e.*, in a lowered

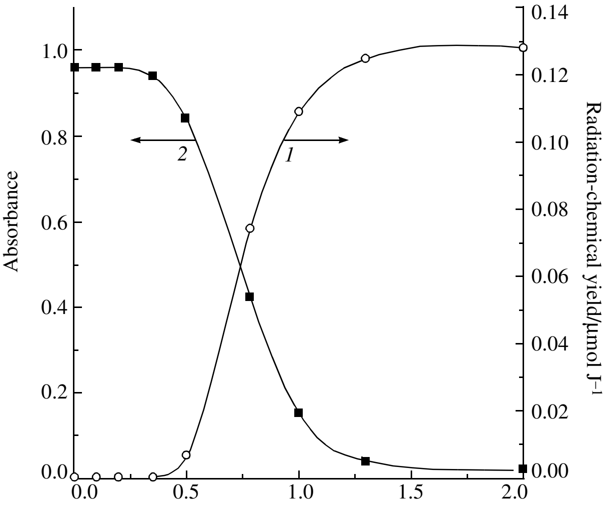

Figure 1 Effect of formate concentration on (*1*) the radiation-chemical yield of oxalate in the absence of nitrate and (*2*) the on combined optical absorption of NO_3^- and NO_2^- ions at 202 nm in the presence of 1×10^{-4} mol dm^{-3} nitrate in an aerated aqueous solution at a dose of 2 kGy.

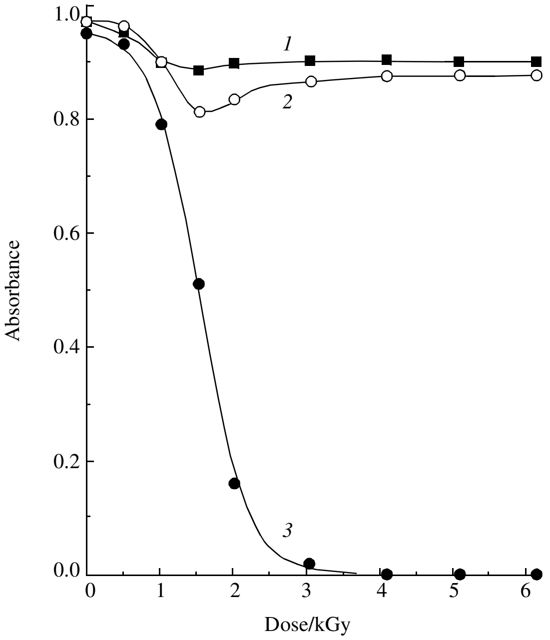

Figure 2 Dose dependence of the combined optical absorption of NO_3^- and NO_2^- ions at 202 nm in aerated aqueous solution (1×10^{-4} mol dm^{-3} nitrate) at initial formate concentrations: (*1*) 2×10^{-4}; (*2*) 5×10^{-4} and (*3*) 1×10^{-3} mol dm^{-3}.

yield of oxalate. Moreover, a part of CO_2^- radical anions can decay in reduction processes such as[6,11]

$$CO_2^- + NO_2^{\cdot} \longrightarrow NO_2^- + CO_2 \quad (k \geq 6\times10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}) \tag{10}$$

$$CO_2^- + N_2O + H_2O \longrightarrow N_2 + CO_2 + {}^{\cdot}OH + OH^- \quad (k = 1.6\times10^3\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}) \tag{11}$$

Reaction (11) is similar to the reaction of N_2O reduction by hydrated electron.[1] Reaction (10) is more significant than reaction (11). This is primarily due to the high rate constant of reaction (10); in addition, the majority of redox processes in the irradiated nitrate–nitrite system proceed through a stage of $NO_2^{\cdot}$ radical formation.[4,5,12]

Figure 2 indicates that at a formate concentration of 2×10^{-4}–5×10^{-4} mol dm^{-3} the removal of nitrate was almost not observed up to a dose of 6.2 kGy. A small decrease in the absorbance at 0.5–2 kGy (curves *1* and *2*) is caused by partial transformation of nitrate to nitrite. The molar absorption coefficient of nitrite is lower than that of nitrate by a factor of about 2, and the maximum of its optical absorption is shifted to 208–209 nm. However, at a deficiency of formate, a scavenger of OH radicals, reduction process (1) is limited, and the major part of nitrite is reoxidised to nitrate. The total efficiency of nitrate degradation under these conditions is lower than 10% and almost independent of dose.

In the presence of more than 8×10^{-4} mol dm^{-3} formate, the dose essentially affected nitrate degradation. At a dose higher than 1 kGy, nitrate has a maximal response to irradiation and is irreversibly decomposed. At a formate concentration of 1×10^{-3} mol dm^{-3} and doses higher than 2 kGy, nitrate decayed almost completely (Figure 1, curve *2*). The radiation-chemical yield of its decomposition under these conditions is 0.067 μmol J^{-1}. In a deaerated solution, the yield[5] was 0.077 μmol J^{-1}. Apparently, this difference in the yields is caused by residual oxygen and, as a consequence, an important role of back oxidation reactions in an aerated solution in comparison with a deaerated solution. In aerated solutions, process (1) can be depressed by reactions (7) and (8). In turn, the OH radical is less sensitive to oxygen. In a deficiency of a scavenger, the radical can easily convert products of reduction (1) back to nitrate in reaction (2).

The results of this study suggest that, in the presence of dissolved oxygen, formate as a scavenger of OH radicals also promotes the radiolytic removal of nitrates and nitrites from aqueous solutions. However, the higher initial concentration of formate is necessary for complete decomposition of nitrate in aerated solutions; an optimal ratio between formate and nitrate concentrations should be about 10. Formate, because of its low radiolytic stability, is not accumulated in the irradiated solution; it undergoes irreversible decomposition. Thus, formate is a promising reagent for the degradation of pollutants by radiolytic reduction in both aerated and deaerated aqueous systems.

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