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# Effect of formate on the radiolytic degradation of nitrate in deaerated aqueous solutions

**Alexandr V. Ponomarev, Alexei V. Bludenko and Igor E. Makarov***

*Institute of Physical Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 429 9244*

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Nitrate ions are irreversibly reduced in dilute aqueous solutions in the presence of formate under the action of an electron beam.

Nitrate and nitrite ions are abundant components of industrial and municipal wastewater. High solubility, stability and toxicity of nitrates and nitrites make their removal from wastewater vital, and this is one of the most difficult environmental problems. Unfortunately, the traditional methods of wastewater treatment appear insufficiently effective to decompose nitrates and nitrites. Earlier,[1] it was found that in aqueous solutions the irreversible removal of nitrate and nitrite can be performed under the action of an electron beam in the presence of effective scavengers of OH radicals. Sulfite was considered as a scavenger.

In actual practice, sulfite is not an optimal supplementary reagent for the removal of nitrite and nitrate because it is an unwanted water pollutant. Under radiolysis, a significant part of sulfite is transformed to less harmful sulfate. However, the total surplus mineralization of water caused by additional sulfite and sulfate is practically not eliminated by radiolytic treatment. It is reasonable to produce the combined presence of nitrate and sulfite by mixing two wastewater types enriched by nitrate and sulfite, respectively. The application of dry sulfite or its concentrated solution is frequently unreasonable because of an unavoidable increase in the mineralization of nitrate-containing wastewater under treatment.

As a rule, the supplementary scavenger should not aggravate the properties of wastewater, and it should fit the following basic requirements: (i) harmlessness — the products of radiolytic conversion of the scavenger should be non-toxic and inert; (ii) availability — the scavenger should not be expensive and limited; (iii) productivity — the required effect should be reached by a minimum amount of the scavenger at a minimum applied dose.

In this work, we used the formate ion as a scavenger of OH radicals to study the mechanism of nitrate decomposition. Formate, similarly to sulfite, has a high reactivity to OH radicals (for sulfite, $k = 1.5\times10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$):

$$\mathrm{OH} + \mathrm{HCOO^-} \rightarrow \mathrm{H_2O} + \mathrm{COO^-} \qquad k = 3.1\times10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{1}$$

and is inert to the reducing products of water radiolysis.[2–4] The rate constant of hydrated electron reaction with formate does not exceed $1\times10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$, and the reaction of formate with the H atom is one order of magnitude slower than reaction (1):

$$\mathrm{H} + \mathrm{HCOO^-} \rightarrow \mathrm{H_2} + \mathrm{COO^-} \qquad k = 3.0\times10^8\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{2}$$

Moreover, formate is not resistant to radiation, and it is irreversibly decomposed to $CO_2$ and $H_2O$.[3,4] That is, the use of formate should cause, in particular, smaller mineralization of wastewater. Thus, formate is a more promising scavenger of OH radicals than sulfite.

The model solutions were prepared from $NaNO_3$ and HCOOLi of extra pure grade. A Specord M40 spectrophotometer was used for optical measurements. Nitrogen compounds were determined at ambient temperature by standard procedures.[5,6] Oxalic acid (oxalate) was determined using the copper–benzidine complex.[7,8] A U-12F linear accelerator was used as a source of quasi-continuous electron radiation (electron energy of 5 MeV, pulse duration of 2.3 μs, pulsing frequency of 400 Hz and dose rate of 10 Gy s$^{-1}$). The solutions were deaerated by bubbling pure argon for 45 min. The solutions were irradiated in glass ampoules (the solution volume was 10 ml and the volume of a gas phase was 5 ml). For measuring the nitrate (nitrite) concentration, the irradiated solutions were stored at 60 °C for 40 min before analysis to remove volatile nitrogen compounds.

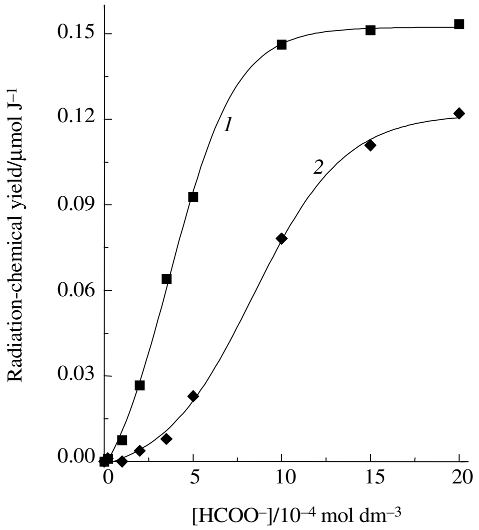

**Figure 1** Influence of formate concentration on the radiation-chemical yield of oxalate formation in aqueous solutions irradiated at 2 kGy: (*1*) without nitrate; (*2*) with $1\times10^{-4}$ mol dm$^{-3}$ nitrate.

One of the final products of the radiolytic conversion of formate in deaerated aqueous solutions is oxalate, the product of combination of ·COO$^-$ radical anions ($2k = 1.5\times10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$).[9] The yield of oxalate in a deaerated aqueous solution increases with initial formate concentration and at a concentration of 0.002 mol dm$^{-3}$ reaches 0.153 μmol J$^{-1}$ (Figure 1, curve *1*). This value indicates the practically complete capture of OH radicals in the bulk of irradiated water after finishing spur processes (0.3 μmol J$^{-1}$)[2,10,11] by formate. It additionally testifies that OH radicals are the main precursors of oxalate ions, and reaction (1) can effectively suppress other processes with the participation of OH radicals. In the presence of nitrate ($1\times10^{-4}$ mol dm$^{-3}$),

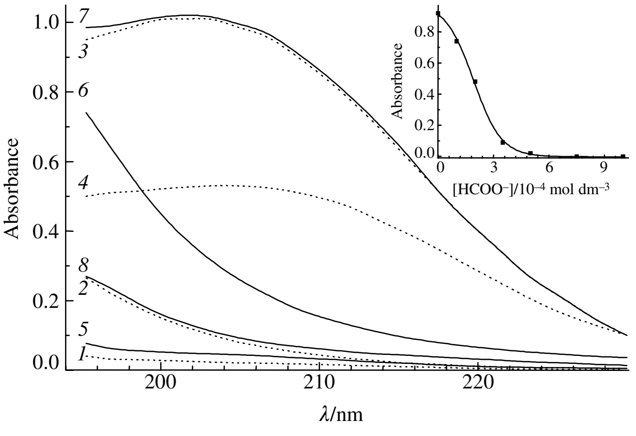

**Figure 2** Optical absorption spectra of initial (*1*, *3*, *5* and *7*) and irradiated (2 kGy) (*2*, *4*, *6* and *8*) deaerated aqueous solutions: (*1*, *2*) $2\times10^{-4}$ mol dm$^{-3}$ formate; (*3*, *4*) $2\times10^{-4}$ mol dm$^{-3}$ formate + $1\times10^{-4}$ mol dm$^{-3}$ nitrate; (*5*, *6*) $5\times10^{-4}$ mol dm$^{-3}$ formate; (*7*, *8*) $5\times10^{-4}$ mol dm$^{-3}$ formate + $1\times10^{-4}$ mol dm$^{-3}$ nitrate. Insert: the influence of formate concentration on the combined optical absorption of $NO_3^-$ and $NO_2^-$ at 202 nm in a $1\times10^{-4}$ mol dm$^{-3}$ nitrate solution at 2 kGy.

the dependence of the radiation-chemical yield of oxalate essentially varies. The noticeable accumulation of oxalate begins only at a formate concentration higher than $3.5\times10^{-4}$ mol dm$^{-3}$. In turn, the limiting yield of oxalate in the presence of nitrate is noticeably lower. It demonstrates an essential effect of small nitrate admixtures on reactions with the participation of OH radicals. Nitrate has a very low activity to OH radicals ($k < < 5\times10^5$ dm$^3$ mol$^{-1}$ s$^{-1}$). The decomposition of nitrate is mainly caused by the reactions with hydrated electrons $e_{aq}^-$ and H atoms:[2,10,11]

$$\mathrm{NO_3^- + e_{aq}^- \rightarrow NO_3^{2-}} \qquad k = 9.7\times10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{3}$$
$$\mathrm{NO_3^- + H \rightarrow HNO_3^-} \qquad k = 1.4\times10^6\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{4}$$
$$\mathrm{NO_3^{2-} + H_2O \rightarrow NO_2^{\bullet} + 2OH^-} \qquad k = 1.0\times10^3\ \mathrm{s^{-1}} \tag{5}$$
$$\mathrm{HNO_3^- \rightarrow NO_2^{\bullet} + OH^-} \qquad k = 2.3\times10^2\ \mathrm{s^{-1}} \tag{6}$$
$$\mathrm{2NO_2^{\bullet} \rightarrow N_2O_4} \qquad k = 7.6\times10^7\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{7}$$
$$\mathrm{N_2O_4 + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+} \qquad k = 1.0\times10^3\ \mathrm{s^{-1}} \tag{8}$$
$$\mathrm{NO_2^{\bullet} + e_{aq}^- \rightarrow NO_2^-} \qquad k = 1.0\times10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{9}$$
$$\mathrm{NO_2^{\bullet} + H \rightarrow H^+ + NO_2^-} \qquad k = 1.0\times10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{10}$$
$$\mathrm{NO_2^{\bullet} + NO \rightarrow N_2O_3} \qquad k = 1.1\times10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{11}$$
$$\mathrm{N_2O_3 + H_2O \rightarrow 2NO_2^- + 2H^+} \qquad k = 5.3\times10^2\ \mathrm{s^{-1}} \tag{12}$$
$$\mathrm{NO_2^- + e_{aq}^- \rightarrow NO_2^{2-}} \qquad k = 4.2\times10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{13}$$
$$\mathrm{NO_2^{2-} + H_2O \rightarrow NO + 2OH^-} \qquad k = 1.0\times10^3\ \mathrm{s^{-1}} \tag{14}$$
$$\mathrm{NO_2^- + H \rightarrow NO + OH^-} \qquad k = 7.1\times10^8\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{15}$$

The difference in the dynamics of oxalate accumulation shown in Figure 1 allows one to propose that the radical anion $\cdot COO^-$ participates in the reducing conversion of nitrate. However, in the deficiency of a scavenger, OH radicals effectively react with the products of reactions (3)–(11) and again convert them to nitrate:[2,10,11]

$$\mathrm{NO_2^- + OH \rightarrow NO_2^{\bullet} + OH^-} \qquad k = 1.0\times10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{16}$$
$$\mathrm{NO_2^{\bullet} + OH \rightarrow HNO_3} \qquad k = 1.0\times10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{17}$$
$$\mathrm{OH + OH \rightarrow H_2O_2} \qquad 2k = 1.06\times10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{18}$$
$$\mathrm{NO_2^- + H_2O_2 \rightarrow NO_3^- + H_2O} \qquad k \le 4\ \mathrm{dm^3\ mol^{-1}\ s^{-1}\ at\ pH\ {\sim}7} \tag{19}$$
$$\mathrm{NO + OH \rightarrow HNO_2} \qquad k = 2.0\times10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{20}$$

A selective scavenger of OH radicals is necessary to suppress these processes. As it can be seen in Figure 1 (curve *2*), a formate concentration higher than $3.5\times10^{-4}$ mol dm$^{-3}$ is sufficient to suppress reactions (16)–(20) by reaction (1).

The kinetics of nitrate and nitrite conversion can be estimated by spectrophotometry (Figure 2). Formate at concentrations of $2\times10^{-4}$ and $5\times10^{-4}$ mol dm$^{-3}$ has rather low absorption at 195–230 nm (curves *1* and *5*). This absorption increases after irradiation due to the higher molar absorption coefficient of oxalate (curves *2* and *6*). Contrary to formate, the smaller amount of nitrate is displayed by an intense band with a maximum at 201–203 nm (curves *3* and *7*). The irradiation of a solution simultaneously containing nitrate and formate to 2 kGy results in a decrease in absorption. In the presence of $2\times10^{-4}$ mol dm$^{-3}$ of formate, the absorption at 202 nm is almost halved (curve *4*), and in the presence of $5\times10^{-4}$ mol dm$^{-3}$ of formate the characteristic absorption band of nitrate disappeared (curve *8*). The residual spectrum in the latter case becomes similar to the spectrum of the irradiated $5\times10^{-4}$ mol dm$^{-3}$ formate solution (curve *6*). As follows from a comparison of curves *6* and *8*, in the presence of nitrate under irradiation, this absorption is lower than that of an individual formate solution. The insert in Figure 2 shows the dependence of the combined optical absorption of $NO_3^-$ and $NO_2^-$ ions in an irradiated $1\times10^{-4}$ mol dm$^{-3}$ nitrate solution on formate concentration. It can be seen that for the almost complete disappearance of the characteristic absorption of nitrate and nitrite at 2 kGy a five-fold excess of formate is required.

Figure 3 indicates that the degradation of nitrate at a formate concentration of $(2–5)\times10^{-4}$ mol dm$^{-3}$ is rather effective. At $5\times10^{-4}$ mol dm$^{-3}$ of formate and a dose of 2 kGy, nitrate is removed practically completely. From the initial slope of curve *2* the yield of nitrate decomposition is estimated at $0.077\pm 0.006$ µmol J$^{-1}$. The same yield is observed at the beginning of curve *1* at a formate concentration of $2\times10^{-4}$ mol dm$^{-3}$. However, in the latter case, the dependence of absorption passes through a minimum at 1–1.5 kGy (about 40% of the initial absorption); then, at 1.5–3 kGy an increase is observed, and at higher doses the absorption is stabilised at a level of 60% of the initial value. A minimum in curve *1* is due to the transformation of a significant part of nitrate to nitrite at doses less than 3 kGy. The formation of nitrite resulted from reactions (8)–(10) and (12). Nitrite is known to exhibit the molar absorption coefficient almost twice lower than that of nitrate. Figure 2 (curve *4*) shows that the optical absorption maximum is shifted to 208–209 nm, being characteristic of nitrite.

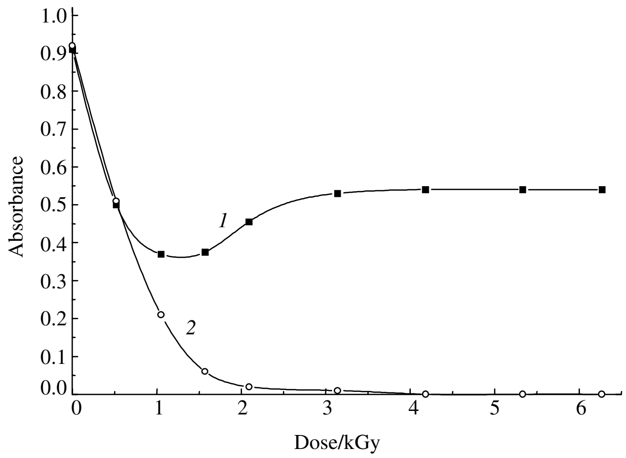

**Figure 3** Dose effect on the combined optical absorption of $NO_3^-$ and $NO_2^-$ ions at 202 nm in a deaerated aqueous solution ($1\times10^{-4}$ mol dm$^{-3}$) of nitrate at an initial formate concentration of (*1*) $2\times10^{-4}$ or (*2*) $5\times10^{-4}$ mol dm$^{-3}$.

The results of this study demonstrate that formate provides rather effective radiolytic removal of nitrates and nitrites from aqueous solutions. Practically complete decomposition of nitrate at a dose of 2 kGy is observed at a 4.5 to 5-fold excess of formate concentration over nitrate. Thus, the efficiency of formate as an OH scavenger is higher than that of sulfite.[1] The presence of formate protects the solution from reverse radiolytic reactions (16)–(20) under irradiation.

Formate is a frequently occurring component of wash water and wastewater (for example, in semiconductor, chemical, papermill and metallurgical industries). Such flows can serve for the dilution of nitrate-containing wastewater and consequent combined electron-beam treatment. In this work, the removal of nitrate under anaerobic conditions was considered. The removal of nitrates under electron-beam treatment in the presence of air seems more reasonable, and it will be discussed elsewhere.

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