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Oxidation of Fe(III) to Fe(VI) by Ozone in Alkaline Solutions

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Abstract—The action of ozone on a suspension of Fe(III) hydroxide in alkaline solutions was studied by the spectrophotometric method. A partial conversion of Fe(III) to Fe(VI) is observed at Fe(III) concentrations exceeding 2 mmol l^{-1}. The tenfold increase of the initial Fe(III) concentration raises the Fe(VI) yield by a factor of 2–3. The mechanism of the process includes the decomposition of ozone with the formation of ozonide ions, which oxidize Fe(III) up to Fe(IV), Fe(V), and Fe(VI) in parallel with their conversion to O_2^- and HO_2^-. Fe(VIII) is not formed.

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The ion FeO_4^{2-} can be obtained by chemical and electrochemical methods, including the action of Cl_2 on Fe(III) hydroxide in alkaline solutions (i.e. by the oxidation with hypochlorite) [1]. A suitable reagent for the synthesis of Fe(VI) could be ozone, which is a stronger oxidizing agent than hypochlorite, as the oxidation potentials of the pairs O_3/O_2 and ClO^-/Cl^- in solutions with pH 14 are 1.24 and 0.89 V, respectively [2]. However the reaction of O_3 with Fe(III) in alkaline conditions remains poorly studied. In the literature there are indications on a possibility to obtain Fe(VI) using ozone [3, 4], but the information on the reaction conditions is restricted. The present work is devoted to a search for conditions providing the formation of Fe(VI) from Fe(III) under the action of ozone.

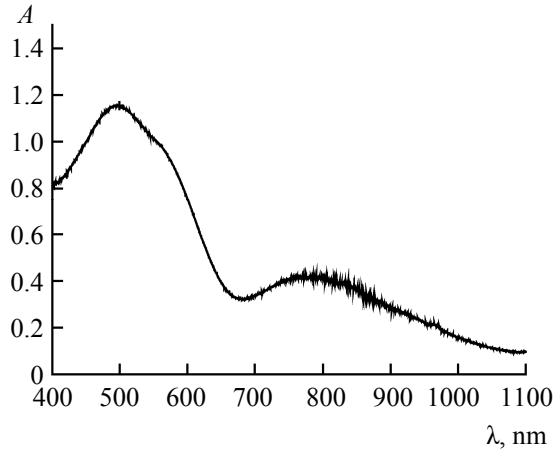
The color of 1–10 M NaOH solutions containing 1 mmol l^{-1} of Fe(III) remains the same after a 3 h ozonation. In solutions with [NaOH] > 10 M a white suspension appears approximately after 5 min passing of ozone. When the ozonation stopped, the suspension gradually disappeared. A minor change in color of 3–10 M NaOH solutions was observed at the Fe(III) concentration of 2 mmol l^{-1}. Solutions of 3–16 M NaOH became red violet when the Fe(III) concentration was 3 and more mmol l^{-1}. The accumulation of Fe(VI) upon the ozonation of 3 mmol l^{-1} Fe(III) solutions within 2 h depends on the alkali concentration as follows:

[NaOH], M	2	3	5	8.5	10	11.4	16
[Fe(VI)], mmol l^{-1}	0.12	0.34	0.80	0.92	1.00	1.00	1.21

An increase in the alkali concentration favors the Fe(VI) formation, though the solubility of ozone decreases on passing from 2 to 16 M NaOH solution.

A spectrum of Fe(VI) obtained by ozonation of a suspension of Fe(III) hydroxide in 8 M NaOH solution [unreacted Fe(III) was separated by centrifugation] is shown as an example in the figure. This spectrum is comparable with the spectrum presented in [5].

Selected data on the accumulation of Fe(VI) in time upon the ozonation of alkaline solutions containing various amount of Fe(III) hydroxide are presented in the table.



Spectrum of Fe(VI) obtained by ozonation of a Fe(III) hydroxide suspension in 8 M NaOH solution [unreacted Fe(III) was separated by centrifugation].

The table shows that it is sufficient to carry out the ozonation in a 3 M NaOH solutions within 0.5–1 h and in 8 solutions NaOH, within 2 h. The increase in the Fe(III) concentration from 3 up to 30 mmol l^{-1} in 3 M NaOH solution almost twice increases the Fe(VI) yield; in a 8 M NaOH solution the Fe(VI) yield increases more than by a factor of three. The fractional addition of Fe(III) to an ozonated solution should be more effective than the creation of a high initial Fe(III) concentration. In fact, the fractional addition of 0.1 M $Fe(NO_3)_3$ solution to the NaOH solution has allowed us to obtain 6 mmol l^{-1} of Fe(VI) for 65 min at final concentrations of NaOH 9 M and Fe(III) 18 mmol l^{-1}.

Effect of conditions on the Fe(VI) yield in the ozonation of alkaline solutions containing a Fe(III) hydroxide suspension

[NaOH], M	[Fe(III)], M	Time, min	[Fe(VI)], M
2	3	30	0.15
		62	0.15
		93	0.12
		123	0.12
2	10	30	0.15
		60	0.19
		100	0.23
3	3	33	0.29
		66	0.30
		97	0.40
		129	0.33
3	10	50	0.42
3	30	30	0.47
		60	0.50
		100	0.57
8	3	31	0.59
		64	0.69
		96	0.82
		128	0.92
8	10	30	1.19
		60	1.8
		90	1.67
		122	1.75
8	30	30	1.25
		62	2.44
		93	2.78
		123	3.23

In 2–11.5 M KOH solutions or in 3–5 M LiOH solutions Fe(III) hydroxide is also partially converted to Fe(VI) compounds under the action of ozone.

Three schemes of ozone decomposition in alkaline solutions are considered [6].

$$\text{(I): } O_3 + OH^- \rightarrow O_2^- + HO_2, \quad (1)$$

$$HO_2 \leftrightarrow H^+ + O_2^-, \quad (2)$$

$$O_3 + O_2^- \rightarrow O_3^- + O_2, \quad (3)$$

$$\text{(II): } O_3 + OH^- \leftrightarrow HO_2^- + O_2, \quad (4)$$

$$O_3 + HO_2^- \leftrightarrow OH + O_2^- + O_2, \quad (5)$$

$$O_3 + O_2^- \rightarrow O_3^- + O_2, \quad (6)$$

$$\text{(III): } O_3 + OH^- \leftrightarrow O_3^- + OH. \quad (7)$$

Scheme(II) is proved in [6]. It is supported in the works [7–9] with the difference that reaction (8) is supposed instead of reaction (5).

$$O_3 + HO_2^- \rightarrow O_3^- + HO_2. \quad (8)$$

The ozonide ion is unstable and decomposes to form O_2^- and HO_2^-. The mechanism of the ozonide ion decomposition was studied in a great number of works, but these studies were fulfilled in weakly alkaline solutions. In a wide range of OH^- concentrations it was done in the work [10].

The O_3^- ion was obtained by the pulsing photolysis of hydrogen peroxide (1.3×10^{-5}–2×10^{-3} M in aqueous alkaline solutions at 27±2°C). The decomposition of O_3^- occurred by first-order reaction (9).

$$O_3^- \rightarrow \text{Products}. \quad (9)$$

Rate constants increased with increasing H_2O_2 concentration and decreased with increasing concentration of alkali or dissolved oxygen. The extrapolation to the zero H_2O_2 concentration (O_2 pressure of 0.2 atm) allows us to estimate the first order rate constant $k(O_3^-)$ for O_3^- decomposition:

[NaOH], M	9.5	4.75	0.95	0.0475	0.0095	pH 10.8
$k(O_3^-)$, s^{-1}	2	40	80	160	650	1100

It was shown in [11] that O_3^- is stabilized in 10^{-8} M KOH solutions at –70 to –30°C that makes it possible to study its behavior by the usual spectrophotometric method. The disintegration of O_3^- is the first-order reaction with a half-life period of 93, 19, and 2.1 min

at –60, –50, and –36°C. The extrapolation to 25–27°C gives the value of the half-life period of ~0.14 s, i.e. $k(O_3^-)$ is ~5 s^{-1}, which coincides completely with the data of [10]. The ozonide ion in parallel with the participation in the decomposition reaction oxidizes Fe(III) hydroxide colloidal particles or $Fe(OH)_4^-$ ions.

$$Fe(OH)_3 + O_3^- + H_2O \rightarrow Fe(OH)_4 + O_2 + OH^-, \quad (10)$$

$$Fe(OH)_4 + O_3^- + 2OH^- \rightarrow FeO_4^{3-} + O_2 + 3H_2O, \quad (11)$$

$$FeO_4^{3-} + O_3^- + H_2O \rightarrow FeO_4^{2-} + O_2 + 2OH^-. \quad (12)$$

The oxidation becomes possible when $k_9[Fe(III)] > k(O_3^-)$. It is seen from the table that Fe(VI) is formed in 2 M NaOH solution containing 3 mmol l^{-1} of Fe(III). The interpolation of $k(O_3^-)$ values in 4.75 and 0.95 M NaOH solutions gives the value of 60 s^{-1} for the 2 M NaOH solution. If $k(O_3^-)$ decreases proportionally to the increase in the O_2 pressure, it is expected to be 12 s^{-1} in pure oxygen. Hence, k_9 ~4×10^3 l mol^{-1} s^{-1}. At a Fe(III) concentration below 3 mmol l^{-1} or in a solution with [NaOH] < 2 M ozonide ions decompose preferentially to form O_2^- and then HO_2^-, which react with both ozone and Fe(VI).

We attempted to react Fe(III) with ozone in an alkaline solution in the presence of periodate ions. It was supposed that these ions are capable to form molecular-disperse complexes either with Fe(III) or with Fe(IV), and such complexes will be oxidized by ozonide ions faster than Fe(III) and Fe(IV) hydroxides. However, in a 10.5 M NaOH solution containing 3 and 6 mmol l^{-1} of Fe(III) and I(VII), respectively, the barbotage within 66 min has not led to the Fe(VI) appearance.

It was shown in [12] that in a 7–11.5 M KOH solution reaction (13) occurs.

$$Fe(OH)_4^- + 3Fe(CN)_6^{3-} + 4OH^- = FeO_4^{2-} + 3Fe(CN)_6^{4-} + 4H_2O. \quad (13)$$

Furthermore, we have found that O_3 and O_3^- oxidize $Fe(CN)_6^{4-}$ up to $Fe(CN)_6^{3-}$.

$$Fe(CN)_6^{4-} + O_3^- + H_2O \rightarrow Fe(CN)_6^{3-} + O_2 + 2OH^-. \quad (14)$$

If reaction (13) is carried out with bubbling ozone, $Fe(CN)_6^{3-}$ will be continuously formed due to reaction (14).

Cyanide complexes of Fe(III) favor a certain increase in the Fe(VI) yield.

We attempted to use MnO_4^- ions as a peculiar catalyst of the Fe(III) oxidation by ozone in 2–12 M NaOH solutions. In alkaline solutions MnO_4^- is converted to MnO_4^{2-} rather fast, but on the action of ozone MnO_4^{2-} is readily oxidized up to MnO_4^-. However it appeared that MnO_4^- oxidizes Fe(III) neither in the absence of ozone nor on its bubling. The difference in the behavior of $Fe(CN)_6^{3-}$ and MnO_4^- is connected with the fact that $Fe(CN)_6^{3-}$ ions replace a certain number of OH^- groups in Fe(III) hydroxide, and an intramolecular charge transfer takes place in the resulting complex. Owing to a weak complex-formation ability, the MnO_4^- ion (similarly to the ClO_4^- ion) does not enter in the reaction of OH^- group replacement and cannot be the oxidizing agent for Fe(III) hydroxide.

We connected a bubbler with 5 M HCl solution to a bubbler with an alkaline solution of Fe(III) + Fe(VI). It was expected that, if O_3 or O_3^- is capable to oxidize FeO_4^{2-} up to FeO_4, which is an analog of OsO_4 and RuO_4, FeO_4 should be carried away by a gas stream and should be absorbed by the HCl solution, transforming to $FeCl_3$, which would tincture the solution. However the color of the HCl solution has not changed upon the ozonation of 3–40 mmol l^{-1} Fe(III) in 2–16 M NaOH solutions. It is known [13] that Am(VI) in an alkaline solution is converted to Am(VII) under the action of ozone, and the potential of the Am(VII)/(VI) pair is 1.050 V. Hence, the potential of the Fe(VIII)/(VI) pair is higher than this value.

In summary it is necessary to note that the effectiveness of the ozone use is rather low, but it can be raised if the ozonation is carried out at –10 to –70°C, as at such temperatures the stability of ozonide-ions would be sufficient for it to react with Fe(III) and not to disappear in side reactions. Validity of such supposition should be shown experimentally.

EXPERIMENTAL

Solutions of special-purity grade $LiOH\cdot H_2O$, concentrated solutions of special-purity grade KOH and NaOH, and chemically-pure and analytical-grade $Fe(NO_3)_3\cdot 9H_2O$ and other reagents were used in the work. Working solutions were prepared using twice-distilled water.

a. In a glass bubbler 3–5 ml of alkali solution was poured and an ozone-oxygen mixture was bubbled at a rate of 10–15 l h^{-1}. The mixture was preliminarily passed through a flask with water to be saturated by water vapor and to avoid a decrease in the volume of a solution in a bubbler with alkali. The concentration of

ozone in the gas mixture was approximately 4 vol % (80 mg of O_3 in 1 l). Aliquots of a $Fe(NO_3)_3$ solution were periodically added in the alkaline solution. If the solution became red violet, solution samples of 0.3–0.5 ml together with a Fe(III) hydroxide suspension were taken and centrifuged in a glass test tube. The solution was transferred to a glass cell with an optical thickness of 0.1 cm, and optical absorption spectra in the range of 400–1000 nm were recorded on a Shimadzu UV 3100 spectrophotometer (Japan).

b. The solution, 0.05–0.1 ml, was mixed with 2.5 ml of a 2 M NaOH solution and a spectrum was recorded in a cell (*l* 1 cm). The concentration of FeO_4^{2-} was estimated by the maximum of the absorption band at 505–510 nm (ε_{510} 1150 l mol^{-1} cm^{-1} [5]).

c. A 16 M NaOH solution, 3 ml, and 0.1 M $Fe(NO_3)_3$ solution and 0.5 M $K_3Fe(CN)_6^{3-}$ solution, 0.03 ml each, were poured in a bubbler. After 5 min when the solution turned red violet, we started to pass an ozone-oxygen mixture. Periodically (once every 3–5 min) 0.2 ml of a 0.1 M $Fe(NO_3)_3$ solution was added in a bubbler (the total of 2 ml). After 68 min the ozonation was stopped. By this moment 9 mmol l^{-1} of Fe(VI) has been collected.

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REFERENCES

1. *Handbuch der Praparativen Anorganischen Chemie*, Brauer, G., Ed., Stuttgart: Ferdinand Enke Verlag, 1980.
2. Bratsch, S.G., *J. Phys. Chem. Ref. Data*., 1989, vol. 18, no. 1, p. 1.
3. Mailfert, M., *Compt. Rend*., 1882, vol. 94, p. 860.
4. Perfiliev, Y.D., Benko, E.M., Pankratov, D.A., Sharma, V.K., and Dedushenko, S.K., *Inorg. Chim. Acta*, 2007, vol. 360, no. 8, p. 2789.
5. Bielski, B.H.J. and Thomas, M.J., *J. Am. Chem. Soc*., 1987, vol. 109, no. 25, p. 7761.
6. Stachelin, J. and Hoigné, J., *Environ. Sci. Technol*., 1982, vol. 16, no. 10, p. 676.
7. Forni, L., Bahnemann, D., and Hart, E.J., *J. Phys. Chem*., 1982, vol. 86, no. 2, p. 255.
8. Tomiyasu, H., Fukutomi, H., and Gordon, G., *Inorg. Chem*., 1985, vol. 24, no. 19, p. 2962.
9. Fábián, I., *Pure Appl. Chem*., 2006, vol. 78, no. 8, p. 1559.
10. Landi, V.R. and Heidt, L.J., *J. Phys. Chem*., 1969, vol. 73, no. 7, p. 2361.
11. Kazarnovskii, I.A., Gorbenko-Germanov, D.S., and Kozlova, I.V., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1969, no. 1, p. 197.
12. Shilov, V.P. and Gogolev, A.V., *Zh. Obshch. Khim*., 2009, vol. 79, no. 9, p. 1417.
13. Krot, N.N., Gel'man, A.D., Mefod'eva, M.P., Shilov, V.P., Peretrukhin, V.F., and Spitsyn, V.I., *Semivalentnoe sostoyanie neptuniya, plutoniya, ameritsiya* (Septivalent State of Neptunium, Plutonium, Americium), Moscow: Nauka, 1977.