## **Reaction of Ozone with Uranium(IV) Oxalate in Water**

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Abstract—Decomposition of aqueous suspensions of uranium(IV) oxalate under the action of an ozone– oxygen mixture was studied. The process occurs in two steps. In the first step, the U(IV) oxidation with the formation of oxalic acid uranyl solutions prevails. The second step involves decomposition of oxalate ions and hydrolysis of uranyl ions. An increase in temperature accelerates the transformation of uranium(IV) oxalate into uranium(VI) hydroxide compounds. In solutions containing KBr or UO<sub>2</sub>Br<sub>2</sub>, the following reaction occurs: O<sub>3</sub> + Br<sup>-</sup>  $\rightarrow$  O<sub>2</sub> + BrO<sup>-</sup>. The arising hypobromite ions and hypobromous acid oxidize uranium(IV) oxalate extremely efficiently. The possible mechanism of ozonation of aqueous uranium(IV) oxalate suspensions is discussed.

Keywords: uranium, ozone, uranium oxalate

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Precipitation of tri- and tetravalent f elements in the form of oxalates allows deep purification of rare earth elements and actinides to remove the majority of d elements [1]. It seems promising to use oxalates of these elements as starting compounds for the synthesis, because they contain no other metals, in contrast to using hydroxides of f elements in various valence states, which are precipitated most frequently with alkali metal and ammonium hydroxides. However, high stability of simple and complex oxalates complicates their further use for preparing compounds with other anions. The problem of removing organic anions and preserving the purity of f elements can be solved by using ozone as a salt-free oxidant. The use of gaseous ozone and low solubility of oxalates of tri- and tetravalent f elements in water complicate decomposition of oxalate anions. For choosing the optimum conditions, it is necessary to use experimental data, lacking today.

Oxidation of poorly soluble U(IV) compounds can favor the formation of more soluble U(VI) compounds. Therefore, knowledge of the specific features of the  $U(C_2O_4)_2 \cdot xH_2O$  oxidation in neutral or close-to-neutral media can be useful for predicting the uranium migration in the environment [2]. Oxidation of uranium(IV) oxalate in neutral aqueous media was not studied in detail. The use of oxygen as oxidant is inefficient because of low solubility of uranium(IV) oxalate. The ozone–oxygen mixture allows acceleration of the oxidation, does not introduce additional substances into the reaction mixture, and is used for oxidation of various compounds in aqueous and nonaqueous media [3, 4].

## EXPERIMENTAL

We used HClO<sub>4</sub>, KHCO<sub>3</sub>,  $K_2C_2O_4$ , and  $H_2C_2O_4$  of chemically pure or analytically pure grade. Potassium bromate (analytically pure grade) was recrystallized twice from water. Uranium(IV) oxalate  $U(C_2O_4)_2$ .  $nH_2O$  was prepared by adding  $H_2C_2O_4$  to a hydrochloric acid U(IV) solution heated to 90°C. The precipitate was heated for 30 min on a water bath [1]. The product composition was in good agreement with the formula  $U(C_2O_4)_2$ ·6H<sub>2</sub>O. Uranyl oxalate  $UO_2C_2O_4$ ·3H<sub>2</sub>O was prepared from an aqueous solution of uranyl nitrate and oxalic acid and was dried in air. Uranium(IV) tetrafluoride was precipitated from a solution of U(IV) in 0.2 M HCl with hydrofluoric acid, washed three times with cooled water to neutral pH value, and dried at 100°C in air. An ozone–oxygen mixture containing ~4 vol % O<sub>3</sub> was bubbled through aqueous suspensions and solutions at a rate of  $10-15 \text{ L} \text{ h}^{-1}$ . The suspensions were clarified on a PE-6910 laboratory centrifuge.

The pH values were measured with an OP-211/1 pH meter equipped with a glass combined electrode.



Fig. 1. Optical density at 419 nm of a solution initially containing 25.5 mg of  $U(C_2O_4)_2$ ·6H<sub>2</sub>O in 5 mL of H<sub>2</sub>O as a function of ozonation time at 22°C. The pH values of the solution are indicated in parentheses.

The ozonized solutions were stored in the dark between the analytical operations.

The concentration of uranium ions was monitored with a Shimadzu UV 3100 spectrophotometer using a cell with an optical path length of 1 cm.

Preliminary experiments have shown that ozonation of U(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O suspensions occurs in weakly acidic and close-to-neutral aqueous media. U(VI) ions exist in such solutions mainly in the form of oxalate complexes or in the hydrolyzed form. For a 0.013 M UO<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + 0.013 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution,  $D_{419} = 0.23$ ,  $\epsilon_{419} = 17.7$  L mol<sup>-1</sup> cm<sup>-1</sup> (Fig. 1). The observed value of  $\epsilon$  is the mean of the  $\epsilon$  values of 16.4 and 19.7 L mol<sup>-1</sup> cm<sup>-1</sup>, estimated from the figure and calculated in [5] for the hydrated complexes UO<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and UO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sup>2–</sup>, respectively.

The extinction coefficient for hydrolyzed uranyl species strongly depends on the experimental conditions and can vary in the course of slow hydrolysis and polymerization reactions. Therefore, for monitoring the concentration of uranyl ions, we recorded their electronic absorption spectra after introducing an aliquot of the ozonized solution into 1.2 M HClO<sub>4</sub> or into a saturated KHCO<sub>3</sub> solution. The extinction coefficients  $\varepsilon$  of U(VI) ions in perchloric acid and bicarbonate solutions for the spectrophotometer used were determined in special experiments. For  $UO_2(H_2O)_5^{2+}$  and  $UO_2(CO_3)_3^{4-}$ , we obtained the  $\varepsilon$  values equal to 8.3 and 28.5 L mol<sup>-1</sup> cm<sup>-1</sup> for  $\lambda = 414$  and 449 nm, respectively. These values virtually coincide with those known from the literature, 8.1 [6] and 29  $\pm$  0.7 L mol<sup>-1</sup> cm<sup>-1</sup> [7]. Close value of  $\varepsilon$  for UO<sub>2</sub>(H<sub>2</sub>O)<sup>2+</sup><sub>5</sub> is also given in the figure in [8].

## **RESULTS AND DISCUSSION**

Bubbling of ozone–oxygen mixture through an aqueous suspension of uranium(IV) oxalate leads to its complete dissolution and formation of a transparent yellow solution. Further ozonation leads to precipitation of yellow substances. The time required for dissolution of the gray-green suspension and precipitation of yellow substances depends on the uranium(IV) oxalate amount, temperature, and presence of additives. Our results show that two steps can be distinguished in ozonation of an aqueous suspension of uranium(IV) oxalate. In the first step,  $U(C_2O_4)_2$  is predominantly oxidized to  $UO_2C_2O_4$ , with partial decomposition of oxalate ions also possible. In the second step, oxalate ions and oxalic acid decompose with the precipitation of uranyl hydrolysis products.

The first step of oxidation of  $U(C_2O_4)_2$  with ozone can be described by the following reaction equation:

$$U(C_2O_4)_2 + O_3 + H_2O \rightarrow UO_2C_2O_4 + H_2C_2O_4 + O_2.$$
(1)

A typical dependence of the concentration of  $UO_2C_2O_4$  formed in reaction (1) on the ozonation time is shown in Fig. 1.

Dissolution of uranium(IV) oxalate is accompanied by the release of oxalic acid and decrease in pH. For ozonized solutions after the dissolution of the suspended material, pH depends on the amount of uranium(IV) oxalate taken and approximately corresponds to pH of the model solutions. For 0.01 M  $H_2C_2O_4$ , pH is 1.97; 0.01 and 0.005 M UO<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solutions have pH 4.06 and 4.08, respectively. The 9.7 ×  $10^{-3}$  M UO<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + 0.01 M  $H_2C_2O_4$  solution has pH 1.82. The transparent yellow solutions formed by ozonation of the suspension have the electronic absorption spectra typical of uranyl complexes (Fig. 2).

The maximum of the strongest absorption band is shifted to 419 nm, and the spectra can be assigned to uranyl oxalate complexes [5, 9]. Complete dissolution of hydrated U(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> occurs also when the solubility of the formed UO<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is exceeded, suggesting the formation of soluble oxalate complexes UO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub><sup>2-</sup>.

As seen from Table 1, oxidation of relatively small amounts of aqueous suspensions of uranium(IV) oxalate with ozone occurs slowly even at elevated temperatures.

To compare, we performed ozonation of a suspension of one more insoluble U(IV) compound,  $UF_4$ . Oxidation of 0.0068 g of  $UF_4$  was complete in 60 min. The solution spectra corresponded to the spectra of uranyl fluoride complexes; the solutions had pH  $\approx$  2.87. Because fluoride ions do not react with ozone, we can conclude that UF<sub>4</sub> quantitatively transformed in accordance with Eq. (2):

$$UF_4 + O_3 + H_2O \rightarrow UO_2F_2 + 2HF + O_2, \qquad (2)$$

$$UO_2F_2 + 2 HF \rightleftharpoons UO_2F_n^{(2-n)+} + 2H^+ + (4-n)F^-.$$
 (3)

The positions of the maxima in the electronic absorption spectra of the solutions (Fig. 2) prove the presence of uranyl fluoride complexes in the solution, and the spectrum agrees with that of a mixture of complex species  $UO_2F_n^{2-n+}$  (n = 1, 2, 3, 4), given in [8].

Calculations show that oxidation of weighable amounts of uranium(IV) oxalate requires a long time even at elevated temperatures. Furthermore, as will be shown below, further oxidation of oxalic acid and oxalate ions in aqueous solutions requires a still longer time. Therefore, we checked the possibility of accelerating the decomposition of uranium oxalates by introducing bromide or chloride ions into the solution.

As seen from Table 1, uranium(IV) oxalate rapidly dissolves in solutions containing bromide ions, and decreasing temperature to room temperature decelerates the process insignificantly. Apparently, Br<sup>-</sup> ions react with O<sub>3</sub>, and products of this reaction efficiently oxidize  $U(C_2O_4)_2$ . It is known that the products of the reaction of ozone with bromide ions in aqueous solutions are hypobromite, BrO<sup>-</sup>, and bromate, BrO<sup>-</sup><sub>3</sub>, ions [10]. An experiment on oxidation of a suspension of 22.3 mg of uranium(IV) oxalate in 4 mL of a 0.1 M KBrO<sub>3</sub> solution showed that uranium(VI) oxalate complexes did not appear in the solution in 45 min at room temperature. Further storage of this solution without stirring for 24 h leads to the appearance of 0.0035 M U(VI) oxalate complexes in the solution. This solution has pH 2.81 and a spectrum characteristic of U(VI) oxalate complexes. Hence, U(IV) is oxidized with bromate ions preferentially with simultaneous release of oxalic acid. Apparently, the reaction with bromate ions cannot ensure the observed rapid oxidation of a  $U(C_2O_4)_2$  suspension with ozone in approximately neutral KBr solutions. Therefore, we conclude that the suspension dissolves owing to the occurrence of the reactions

$$O_3 + Br^- \to O_2 + BrO^-, \tag{4}$$

$$U(C_2O_4)_2 + BrO^- + H_2O \rightarrow UO_2C_2O_4 + H_2C_2O_4 + Br^-.$$
 (5)

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**Fig. 2.** Spectra of (1) a model solution containing 0.013 M  $UO_2C_2O_4$  and 0.013 M  $H_2C_2O_4$  and solutions obtained after ozonation of suspensions of (2) 25.5 mg of  $U(C_2O_4)_2$ ·6H<sub>2</sub>O in 5 mL of H<sub>2</sub>O and (3) 11 mg of UF<sub>4</sub>·H<sub>2</sub>O in 4.5 mL of H<sub>2</sub>O.

Additional experiments on U(IV) oxidation in potassium oxalate solutions with potassium bromate have shown that the consumption of U(IV) oxalate complexes in a homogeneous solution is also slow. For example, in a solution containing 0.0052 M U(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>, 0.05 M K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and 0.05 M KBrO<sub>3</sub>, a pseudo-firstorder reaction with the first half-conversion time of 150 min occurred at 22°C. Deviations from the first order were observed only in the first 15 min, despite a uniform decrease in pH from 6.6 to 5.16 that we noted. The observed rate constant of the reaction U(C<sub>2</sub>O<sub>4</sub>)<sup>2</sup><sub>2</sub> + BrO<sub>3</sub><sup>-</sup> at 22.4°C is  $4.2 \times 10^{-3}$  min<sup>-1</sup>. The U(IV) concentration was monitored using the strongest absorption band with a maximum at 663 nm in the spectrum of

**Table 1.** Time  $\tau_s$  of dissolution of uranium(IV) oxalate suspensions in aqueous solutions under the action of ozone, pH values of the resulting solutions, and positions of the most intense optical absorption maximum  $\lambda_{max}$ 

$\begin{array}{c} \mathrm{U}(\mathrm{C}_{2}\mathrm{O}_{4})_{2} \cdot n\mathrm{H}_{2}\mathrm{O},\\ \mathrm{mg}\ \mathrm{mL}^{-1} \end{array}$	Electrolyte, M	T, ℃	$\tau_{s}$ , min	λ <sub>max</sub> , nm	pН
5.1	_	22	540	418	2.22
UF <sub>4</sub> , 2.4	_	22	60	420	2.87
6.25	_	70	60	419	_
11.8	_	80	120	418	_
5.5	KBr, 0.1	80	10	448	_
5.6	KBr, 0.01	70	10		≥7
5.5	KBr, 0.1	19	10	449	7.57
4.5	KBr, 0.04	22	5		7.48
5.25	$UO_2Br_2, 0.04$	24	15	_	4.26
5.1	NaCl, 0.1	80	25		5.46
4.6	KCl, 0.04	22	150	—	1.83



**Fig. 3.** Spectra of a solution obtained (1) after ozonation of a suspension containing 21 mg of  $U(C_2O_4)_2 \cdot 6H_2O$  in 4 mL of  $4.25 \times 10^{-2}$  M UO<sub>2</sub>Br<sub>2</sub> for 30 min and (2) after precipitated formation. (3) Spectrum of aqueous suspension that initially contained 25.2 mg of  $U(C_2O_4)_2 \cdot 6H_2O$  in 0.1 M KBr after ozonation for 90 min.

the initial solution, coinciding with the published spectrum [11]. The spectrum of the oxidized solution had the shape characteristic of U(VI) oxalate complexes [5, 9] with the most pronounced maximum at approximately 419 nm.

It should be noted that ozonation of aqueous  $U(C_2O_4)_2$  suspensions containing Br<sup>-</sup> occurs virtually without intermediate formation of a transparent yellow solution. Precipitation of a yellow substance starts immediately after dissolution of the initial gray-green suspended material. In some experiments, the gray-green suspended substance transformed into a yellow precipitate without intermediate formation of a transparent solution. Hence, in KBr solutions hypobromite ions efficiently react with oxalate ions.

**Table 2.** Total time  $\tau$  of transformation of aqueous uranium(IV) oxalate suspensions into uranium(VI) hydroxide compounds under the action of ozone

$U(IV)_{0},$ mg mL <sup>-1</sup>	Electrolyte, M	<i>T</i> , ℃	τ	pН
6.25	-	70	7 h	_
11.8	-	80	10 h	5.55
5.5	KBr, 0.1	80	16 min	8.45
5.3	NaCl, 0.1	80	1.5 h	5.46
5.6	KBr, 0.01	70	11 min	≤7
5.7	KBr, 0.1	19	10 min	7.57
5.3	$UO_2Br_2, 0.042$	24	30 min	4.26
_	$UO_2C_2O_4$ , 0.013 + $H_2C_2O_4$ ,	23	>21 h	>3.2
	0.013			
4.5	KBr, 0.04	22	8 min	7.5

Reactions (4) and (5) can be performed without introducing additional cations into the solutions. For example, ozonation of 4.25 mL of a solution containing 0.04 M UO<sub>2</sub>Br<sub>2</sub> and 21 mg of U(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, performed at 25°C for 15 min, leads to a change in the suspension color from gray-green to light yellow. Further ozonation for 15 min allowed preparation of a bright yellow opalescent solution with the spectrum characteristic of hydrolyzed U(VI) (Fig. 3, spectrum *I*). In storage, a light yellow substance precipitated from the solution.

The rate of the reaction of  $O_3$  with  $Cl^-$  increases with a decrease in pH of solutions. Therefore, dissolution of uranium(IV) oxalate accelerates in chloride solutions. However, the performance of chloride additives is low and was not considered in this study in detail.

In our experiments on ozonation of  $U(C_2O_4)_2$  suspensions without additives, the solution spectra after the dissolution completion corresponded to the published spectra of oxalate complexes and in some cases to the spectra of hydrolysis products of uranyl ions [12–14]. Because of the release of oxalic acid in reaction (1), such solutions had pH from 1.8 to 3.

In the second step of the ozonation, oxalic acid and oxalate ions decompose, which leads to an increase in pH. Ozonation of oxalic acid solutions of U(VI) without additives takes a long time (Table 2).

Ozonation leads to the decomposition of oxalate ions in reactions (6)–(8),

$$H_2C_2O_4 + O_3 \rightarrow 2CO_2 + O_2 + H_2O_3$$
 (6)

$$HC_2O_4^- + O_3 \rightarrow 2CO_2 + O_2 + OH^-,$$
 (7)

$$C_2O_4^{2-} + O_3 + H_2O \rightarrow 2CO_2 + O_2 + 2OH^-,$$
 (8)

and to removal of  $CO_2$  with a stream of the ozoneoxygen mixture. Therefore, the  $[C_2O_4^{2-}]/[UO_2^{2+}]$  ratio decreases and pH increases, which leads to the formation of polymeric hydroxo oxalate complexes. Without complexing agents at  $[UO_2^{2+}] \sim 0.01$  M, hydrolysis occurs at pH > 3. Manfredi et al. [14] studied the hydrolysis of  $UO_2^{2+}$  at pH in the interval 2.5–4.5 and formation of hydroxo oxalate complexes at pH in the interval 4.5–8.5. The process completes in precipitation of yellow substances and disappearance of the optical absorption caused by uranium compounds in solution. Table 3 shows how pH of the solution varies in the course of ozonation.

Parameter	Value at indicated $\tau$ , h										
	0	1	3.5	6	8.5	11.5	15.5	16.5	18	18 <sup>a</sup>	21
pН	1.8	1.8	1.86	1.89	1.96	-	2.65	2.8	2.99	3.3	3.2
$D_{419}$	0.23	0.23	0.23	0.236	0.238	0.246	0.234	0.24	0.241	0.241	_

Table 3. Ozonation of a 0.013 M  $UO_2C_2O_4 + 0.013$  M  $H_2C_2O_4$  solution at 23°C

<sup>a</sup> The solution storage in the dark for 21 h led to a change in pH without changes in the optical absorption spectrum.

Owing to decomposition of oxalate ions in reactions (6)-(8) and dissociation of oxalate complexes,

$$UO_2(C_2O_4)_2^{2-} \rightarrow UO_2(C_2O_4) + C_2O_4^{2-}.$$
 (9)

the solubility of uranyl oxalate can be exceeded, which will cause partial precipitation of  $UO_2C_2O_4$ ·3H<sub>2</sub>O. In ozonation of solutions with  $[UO_2C_2O_4] \le 0.01$  M, we recorded the spectra of hydrolyzed U(VI) species (Fig. 3), similar to those presented previously in numerous papers, e.g., in [13, 14].

According to [15], the reaction of  $O_3$  with  $C_2O_4^{2-1}$ ions is so slow that the reaction rate at room temperature cannot be measured. Hydrolysis of uranyl ions occurs at pH in the range 4–5, i.e., in solutions containing predominantly  $HC_2O_4^{-1}$  ions. In the slow ozonation process in solutions with pH < 5, the most probable limiting step is the reaction

$$O_3 + HC_2O_4^- \to O_2 + OH + C_2O_4^-,$$
 (10)

followed by a chain of radical reactions

$$OH + HC_2O_4^- \rightarrow H_2O + C_2O_4^-, \tag{11}$$

$$O_3 + C_2 O_4^- \to O_3^- + 2CO_2,$$
 (12)

$$O_3^- + H^+ \to O_2 + OH. \tag{13}$$

The use of uranyl oxalate solutions for measuring the luminous flux intensity is known for a long time [16]. In particular, photolysis of weakly acidic uranyl oxalate solutions was studied [17]. The possibility of photochemical decomposition of oxalate ions in uranium-containing liquid radioactive waste was considered [18]. Therefore, we attempted to combine ozonation with photochemical decomposition of oxalates, sensitized with uranyl ions. We have found that such combination can be efficient in the step of transparent solutions. In this case, oxidation of oxalate ions with excited uranyl ions occurs simultaneously with ozoneinitiated reactions:

$$UO_2^{2+} + hv \to UO_2^{2+},$$
 (14)

$$UO_2^{2+} + C_2O_4^{2-} \to UO_2^+ + C_2O_4^-,$$
(15)

$$UO_2^+ + O_3 \rightarrow UO_2^{2+} + O_3^-.$$
 (16)

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Apparently, uranyl ions in the dark do not catalyze the reaction of ozone with oxalic acid and oxalates. Evolution of the spectrum of a 0.01 M UO<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution under the action of an ozone-oxygen mixture and of UV radiation (VIO-1 lamp) in a glass bubbler shows that the initial spectrum of uranyl oxalate complexes transforms into the spectrum of hydrolyzed uranium (similar to spectra 1 and 2 in Fig. 3) within 2 h. In the process, pH increases from 4.11 to 4.92. In the subsequent 2 h, the solution spectrum does not change in shape but considerably increases in the intensity, and pH increases to 5.6. Hydrolysis of uranyl ions occurs relatively slowly. The subsequent storage of this solution for 17.5 h in the dark led to precipitation of a yellow substance and to a decrease in pH to 5.04. Similar but faster changes occur in the course of joint photolysis and ozonolysis of a 0.01 M UO<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution in a quartz bubbler. After the lapse of 1 h, the solution spectrum (pH of solution 4.94) contained only the absorption band of hydrolyzed U(VI). In the subsequent 2 h, the intensity of the absorption band of hydrolyzed U(VI) considerably increased, and a fine suspension was formed. After storage of this solution in the dark for 20 h, a pale yellow precipitate was formed. The intensity of the spectrum decreased by a factor of approximately 3, but its shape did not change.

The efficiency of the action of UV radiation decreases owing to precipitation of uranyl oxide– hydroxide compounds in the solution volume and on bubbler walls. Therefore, photolysis does not ensure complete decomposition of oxalic acid and oxalates at acceptable rate, and the use of accelerating additives is necessary. We have studied the effect of bromide and chloride ions.

Decomposition of oxalic acid and its anions efficiently occurs in solutions containing KBr and  $UO_2Br_2$ . Hypobromite ions arise in reaction (4) and are consumed in parallel reactions (17)–(19):

 $H_2C_2O_4 + HOBr \rightarrow 2CO_2 + HBr + H_2O, \qquad (17)$ 

 $C_2O_4^{2-} + HOBr \rightarrow 2CO_2 + Br^- + OH^-,$  (18)

$$HC_2O_4^- + HOBr \rightarrow 2CO_2 + Br^- + H_2O.$$
(19)

The observed process rate is controlled by reaction (19) [19]. According to [20], in solutions with pH 6 the pseudo-first-order rate constants for the reactions of oxalate ions with O<sub>3</sub> and HOBr are  $<8 \times 10^{-7}$ and  $4 \times 10^{-5}$  s<sup>-1</sup>, respectively. Also, the following equilibrium occurs in bromide solutions:

$$Br_2 + H_2O \rightleftharpoons H^+ + Br^- + HOBr.$$
 (20)

Molecular bromine  $Br_2$  (or tribromide anion  $Br_3^-$ ) is less efficient in oxidation of oxalic acid and oxalates. Increasing pH enhances the bromine hydrolysis and accelerates the decomposition. The suspensions and solutions containing KBr after the ozonation completion have pH > 7. On the other hand, in solutions containing UO<sub>2</sub>Br<sub>2</sub>, the process completes in precipitation at pH < 7. The electronic absorption spectra suggest the presence of small amounts of uranyl carbonate complexes in such solutions. The most probable explanation to this fact is based on the occurrence of equilibrium reaction (20) in aqueous solution.

After the decomposition of oxalate ions, at pH > 5, the reaction between bromide and bromate ions becomes very slow, and bromate ions are accumulated in the solution. Upon acidification of such solutions, the following reactions occur:

$$BrO_{3}^{-} + 5Br^{-} + 6H^{+} \rightarrow 3Br_{2} + 3H_{2}O,$$
 (21)

$$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr.$$
 (22)

The spectra of the acidified solutions acquire intense yellow color owing to bromine formation.

Molecular bromine is highly volatile at pH < 6 and is removed from the aqueous medium with an ozone– oxygen stream [22]. The removal of Br<sub>2</sub> and decomposition of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> lead to an increase in pH to the values at which the arising CO<sub>2</sub> can form HCO<sub>3</sub><sup>-</sup> ions. Potassium bicarbonate is accumulated in the solutions in an amount sufficient for the formation of soluble uranyl carbonate complexes. The U(VI) concentration estimated from the spectrophotometric data (Fig. 3, spectrum 3) reaches 0.0016 M after the decomposition of 25.2 mg of uranium(IV) oxalate in 5 mL of 0.1 M KBr at 24°C.

Dissolution of hydrolysis products of uranyl ions in 1 M  $HClO_4$  yields solutions whose spectrum is characteristic of uranyl aqua ions. No precipitates are formed on adding a thorium nitrate solution to such solutions. Hence, the precipitates contain no weighable amounts of oxalate ions.

As seen from Table 2, chloride ions also accelerate decomposition of oxalate ions and oxalic acid, but their performance is considerably lower than that of KBr. This may be due to considerably lower rate of the reaction of  $O_3$  with Cl<sup>-</sup>, especially in solutions with pH > 3. Therefore, we have not studied the ozonation of U(VI) chloride–oxalate solutions in detail.

The results of our study show that ozonation of suspensions of uranium(IV) oxalate can yield oxalic acid U(VI) solutions. The decomposition considerably accelerates in the presence of KBr. The UF<sub>4</sub> suspension also reacts with an ozone–oxygen mixture to form hydrofluoric acid U(VI) solutions. Decomposition of oxalic acid and uranium(VI) oxalate also considerably accelerates in solutions containing KBr or UO<sub>2</sub>Br<sub>2</sub>. The ozonation completes in hydrolysis of uranyl ions and precipitation of U(VI) oxide–hydroxide compounds. Prolonged ozonation of aqueous suspensions of uranium(IV) oxalate and of solutions of U(VI) oxalate can be used in the laboratory practice for preparing U(VI) hydroxide compounds free of foreign metal cations.

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