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Kinetics of Technetium Reactions: XV. Tc(IV) Oxidation with Persulfate Ions in $HClO_4$ Solution

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Abstract—Tc(IV) is oxidized with persulfate ions in $HClO_4$ solution by reactions with both $S_2O_8^{2-}$ ion and product of its thermal decomposition, Caro acid, H_2SO_5. The reaction rate at 35°C and solution ionic strength $\mu = 1$ is described by the equation $d[Tc(IV)]/dt = k_1[Tc(IV)][S_2O_8^{2-}] + k_3[Tc(IV)][HSO_5^-]/[H^+]$, where $k_1 = 0.88 \pm 0.04$ l mol^{-1} min^{-1} and $k_3 = 110 \pm 5$ min^{-1}. With increasing ionic strength to $\mu = 2$, both rate constants decrease ($k_1 = 0.58 \pm 0.08$ l mol^{-1} min^{-1} and $k_3 = 52 \pm 2$ min^{-1} at 35°C). The activation energy of the overall reaction is 77.7 ± 8.1 kJ mol^{-1}. The mechanisms of both reactions are discussed.

The technetium ions play an important role in the reprocessing of spent nuclear fuel, accelerating oxidation of Pu(III), U(IV), and hydrazine with nitric acid [1].

In our previous papers, we considered features of the redox reactions of Tc(IV), Tc(V), and Tc(VII) ions predominantly in hydrochloric acid solutions, in particular, reduction of Tc(VII) with hydroxyethylhydrazine [2] and hydroxylamine [3]. The results of these studies were summarized in [4]. The behavior of the technetium ions in nitric and perchloric acid solutions is studied insufficiently, primarily because of problems with the analysis of the technetium oxidation states in these media.

In this work, we studied the kinetics and mechanism of Tc(IV) oxidation with persulfate ions in perchloric acid solutions. The reaction progress was monitored spectrophotometrically; the optical density of TcO^{2+} ions at 325 nm (extinction coefficient ε_{325} = 3800 l mol^{-1} cm^{-1}) was measured. Since at this wavelength the TcO_4^- ions (product of the reaction) also absorb, the Tc(IV) concentration as a function of time was calculated from the difference between the current and final optical densities ($D - D_\infty$) of the solution. It was shown that the $D - D_\infty$ value is proportional to the Tc(IV) concentration. On the whole, the procedure was similar to that used when studying oxidation of Tc(IV) with HNO_2 in $HClO_4$ solution.

Chemically pure grade potassium persulfate was used without additional purification. The other components of the reaction mixtures were the same as in [5].

To confirm high rate of the reaction of $S_2O_8^{2-}$ ions with Tc(V), as an intermediate of Tc(IV) oxidation, we studied the kinetics of this reaction in the HCl solution, in which Tc(V) is stabilized due to formation of the complex ions $TcOCl_5^{2-}$ [6, 7]. The absorption of this ion at 290 nm was used to monitor the reaction. The initial solution of H_2TcOCl_5 in 6 M HCl was prepared from NH_4TcO_4 by the reaction with concentrated HCl at room temperature as in [8].

The changes in the spectrum of the reaction mixture show that the reaction of Tc(IV) with $S_2O_8^{2-}$ ions is accompanied by transition of Tc(IV) into Tc(VII); the absorption of Tc(IV) at 325 nm decreases, and the TcO_4^- bands appear at 290 and 244–248 nm.

The final product of $S_2O_8^{2-}$ reduction with metal ions is sulfuric acid (or, more precisely, hydrosulfate ion HSO_4^-, regarding the predominant dissociation of H_2SO_4 along the first step at relatively high H^+ concentration). Thus, the stoichiometric equation of the overall reaction between Tc(IV) and excess $S_2O_8^{2-}$ ions is as follows:

$$2TcO^{2+} + 3S_2O_8^{2-} + 6H_2O = 2TcO_4^- + 6HSO_4^- + 6H^+. \quad (1)$$

In our work, the kinetics of reaction (1) was studied in perchloric acid solution at the constant ionic strength $\mu = 1$ and 2 ($NaClO_4$), high (100–400-fold) $S_2O_8^{2-}$ excess, and within the 25–40°C temperature range (mainly at 35°C).

Our study showed that this reaction is autocatalytic; its rate increases with time. This is apparently due to the fact that Tc(IV) is oxidized not only with $S_2O_8^{2-}$ ions, but also with the products of their thermal decomposition. In this connection, it is reasonable to consider the published data on the rate and mechanism of this process.

Kolthoff and Miller [9] found that the rate of $S_2O_8^{2-}$ decomposition in the perchloric acid medium within a wide range of pH is described by the equation

$$-d[S_2O_8^{2-}]/dt = k_4[S_2O_8^{2-}] + k_2[S_2O_8^{2-}][H^+], \qquad (2)$$

where $k_4 = 6.0 \times 10^{-5}$ min^{-1} and $k_2 = 3.5 \times 10^{-3}$ l mol^{-1} min^{-1} at 50°C and $\mu = 0.4$. The activation energies of the two reaction pathways amount to $E_4 = 140$ and $E_2 = 108$ kJ mol^{-1}, respectively.

It follows from these data [9] that, in acid solutions (in our case, at $[H^+] > 0.25$ M), $S_2O_8^{2-}$ ions decompose almost exclusively along the pathway with the rate constant k_2, i.e.,

$$-d[S_2O_8^{2-}]/dt = k_2[S_2O_8^{2-}][H^+], \qquad (3)$$

where k_2 recalculated to 35°C is 4.3×10^{-4} l mol^{-1} min^{-1}.

Kolthoff and Miller [9] believe that, at fairly high concentration of H^+ ions, in accordance with Eq. (3), the mechanism of $S_2O_8^{2-}$ decomposition includes the slow stage

$$S_2O_8^{2-} + H^+ \rightarrow SO_4^{\bullet} + HSO_4^-. \qquad (4)$$

Then, $SO_4^{\bullet}$ radicals are hydrated in a fast stage with formation of Caro acid,

$$SO_4^{\bullet} + H_2O \rightarrow H_2SO_5, \qquad (5)$$

which can undergo slow hydrolysis with the release of hydrogen peroxide:

$$H_2SO_5 + H_2O \rightarrow H_2SO_4 + H_2O_2. \qquad (6)$$

It is important for us that the yield of Caro acid even in 2 M $HClO_4$ at 50°C is 95%, whereas the yield of hydrogen peroxide does not exceed 5% [9]. Based on these results, the stoichiometric equation of $S_2O_8^{2-}$ decomposition in $HClO_4$ solutions can be presented as follows:

$$S_2O_8^{2-} + H_2O = HSO_4^- + HSO_5^-, \qquad (7)$$

i.e., 1 mol of the decomposed $S_2O_8^{2-}$ ions gives 1 mol of Caro acid, and the reaction rate is controlled by Eq. (3).

Turning back to the reaction between Tc(IV) and $S_2O_8^{2-}$ ions, we can assume that the self-acceleration of this reaction is caused by oxidation of Tc(IV) with Caro acid. On the other hand, we cannot rule out the possibility of Tc(IV) oxidation directly with $S_2O_8^{2-}$ ions along the noncatalytic pathway, since the rate of the reaction in the initial stage is nonzero.[1] With regard to both reaction pathways, the kinetic equation is

$$-d[\mathrm{Tc(IV)}]/dt = k_1[\mathrm{Tc(IV)}][S_2O_8^{2-}] + k_3[\mathrm{Tc(IV)}][HSO_5^-]. \qquad (8)$$

The reaction order with respect to $S_2O_8^{2-}$ ions found from the initial portions of the kinetic curves is close to 0.6, which is qualitatively confirmed by Eq. (8).

The simplest kinetic dependences are observed on the assumption of fast oxidation of Tc(IV) with Caro acid, when the rate of the autocatalytic reaction pathway is determined by the rate of $S_2O_8^{2-}$ decomposition in accordance with Eq. (3) and is independent of the Tc(IV) concentration. Then, taking into account a large excess of $S_2O_8^{2-}$ ions, we obtain[2]

$$-d[\mathrm{Tc(IV)}]/dt = k_1[\mathrm{Tc(IV)}][S_2O_8^{2-}] + k'_2, \qquad (9)$$

where

$$k'_2 = k_2[S_2O_8^{2-}][H^+]. \qquad (10)$$

Designating the initial Tc(IV) concentration ($[\mathrm{Tc(IV)}]_0$) as a, the current Tc(IV) concentration as $a - x$, and taking into account that in each run $[S_2O_8^{2-}] = \mathrm{const}$, we find that

$$dx/dt = k'_1(a - x) + k'_2. \qquad (11)$$

After separation of variables and integration, we obtain a linear dependence on time:

$$\ln[(a - x) + K] = \ln(a + K) - k'_1 t, \qquad (12)$$

where $k'_1 = k_1[S_2O_8^{2-}]$ and $K = k'_2/k'_1$.

Treatment of the experimental kinetic data by Eq. (12) shows its reasonable adequacy. However, there is a discrepancy between the experimentally found rate constants k'_2 and those calculated from

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[1] Contrastingly, Am(III) oxidation with persulfate ions proceeds only along the catalytic pathway, due to the reaction of Am^{3+} with $SO_4^{\bullet-}$, $SO_4^{\bullet}$, and $HO^{\bullet}$ radicals generated by $S_2O_8^{2-}$ decomposition [10].

[2] Since reaction (7) is independent, the degree of $S_2O_8^{2-}$ decomposition should be estimated. The calculation using Eq. (3) showed that, under the conditions of our experiments, no more than 3% of $S_2O_8^{2-}$ ions is decomposed during the time of complete Tc(IV) oxidation.

Table 1. Dependence of the rate constants k'_1, k'_2, and k'_3 on the $S_2O_8^{2-}$ concentration at 35°C, $[H^+] = 1$ M, and $\mu = 1$ ($[Tc(IV)]_0 = 1.7 \times 10^{-4}$ M)

$[S_2O_8^{2-}]$, M	k'_1, min^{-1}	$k'_2 \times 10^5$, mol l^{-1} min^{-1}	k'_3, l mol^{-1} min^{-1}	k_1,* l mol^{-1} min^{-1}
0.025	0.022	1.10	100	0.88
0.050	0.045	2.15	100	0.90
0.075	0.070	3.20	90	0.93
0.100	0.900	4.30	110	0.90
			Average	0.90 ± 0.05

* $k_1 = k'_1/[S_2O_8^{2-}]$.

Eq. (10) using k_2 obtained in [9]. It turned out that the rate of $S_2O_8^{2-}$ decomposition substantially (by a factor of 16 at $[H^+] = 1$ M, $[S_2O_8^{2-}] = 0.1$ M) exceeds the rate of the Tc(IV) reaction with the Caro acid. Obviously, the latter reaction is not fast, and hence it should be considered to be one of the limiting stages.

Thus, three slow stages

$$2Tc(IV) + S_2O_8^{2-} \rightarrow 2Tc(V) + HSO_4^-, \quad (13)$$

$$S_2O_8^{2-} + H_2O \rightarrow HSO_4^- + HSO_5^-, \quad (7)$$

$$2Tc(IV) + HSO_5^- \rightarrow 2Tc(V) + HSO_4^-, \quad (14)$$

should be taken into consideration when treating the experimental data. Then, assuming that all the three slow stages are the first-order reactions with respect to the reacting ions, we obtain the following system of differential equations:

$$-d[Tc(IV)]/dt = k_1[Tc(IV)][S_2O_8^{2-}] + k_3[Tc(IV)][HSO_5^-], \quad (8)$$

$$d[HSO_5^-]/dt = k_2[S_2O_8^{2-}] - k_3[Tc(IV)][HSO_5^-]. \quad (15)$$

Let us designaate the Tc(IV) consumption in reactions (13) and (14) and formation of HSO_5^- ions by reaction (7) as x, y, and z, respectively. Then Eqs. (8) and (15) are transformed as follows:

$$3\,d(x + y)/dt = k'_1(a - x - y) + k'_3(a - x - y)(z - y), \quad (16)$$

$$d(z - y)/dt = k'_2 - k'_3(a - x - y)(z - y), \quad (17)$$

where $k'_1 = k_1[S_2O_8^{2-}]$ and $k'_2 = k_1[S_2O_8^{2-}]$.

After simplifying the system of Eqs. (16) and (17) by substitution of variables, it was solved numerically using the Mathcad software and experimental kinetic data obtained under various conditions. The first-order rate constants k'_1 of reaction (13) and second-order rate constants k'_3 of reaction (14) were determined after preliminary calculation of the zero-order rate constant k'_2 of reaction (7) by Eq. (10) under the preset experimental conditions. The results of the mathematical treatment are listed in Tables 1 and 2.

As seen from Table 1, the rate constant k'_1 of reaction (13) increases in proportion to the concentration of $S_2O_8^{2-}$ ions, whereas the rate constant k'_3 of reaction (14), as expected, is independent of the concentration of these ions. Thus, at constant $[H^+]$ concentration and constant solution ionic strength, the rate of Tc(IV) oxidation is described by the equation

$$-d[Tc(IV)]/dt = k_1[Tc(IV)][S_2O_8^{2-}] + k'_3[Tc(IV)][HSO_5^-], \quad (18)$$

where $k'_1 = 0.90 \pm 0.04$ l mol^{-1} min^{-1} and $k'_3 = 100 \pm 13$ l mol^{-1} min^{-1} at 35°C, $[H^+] = 1$ M, and $\mu = 1$.

The dependence of the rate constants k'_1 and k'_3 on the $[H^+]$ concentration was studied in an $HClO_4$ + $NaClO_4$ mixed solution at two ionic strength values ($\mu = 1$ and 2). The data obtained (Table 2) show that k'_1 is virtually independent of $[H^+]$, whereas k'_3 is approximately inversely proportional to $[H^+]$. Hence, the overall equation of the rate of the reaction between Tc(IV) and $S_2O_8^{2-}$ ions is as follows:

$$-d[Tc(IV)]/dt = k_1[Tc(IV)][S_2O_8^{2-}] + k_3[Tc(IV)][HSO_5^-]/[H^+], \quad (19)$$

where $k_1 = 0.88 \pm 0.04$ and 0.58 ± 0.08 l mol^{-1} min^{-1} and $k_3 = 110 \pm 5$ and 52 ± 2 l min^{-1} at 35°C and $\mu = 1$ and $\mu = 2$, respectively. These rate constants were calculated as average values from the data of Tables 1 and 2.

The comparison of the above results shows that the reaction rate along both reaction pathways decreases with increasing the solution ionic strength, i.e., the overall reaction is characterized by the negative electrolytic effect.

In conclusion of this part of work, we consider the temperature dependence of the reaction rate. Un-

Table 2. Dependence of the rate constants k'_1, k'_2, and k'_3 on the H^+ concentration in the $HClO_4$ + $NaClO_4$ solution at $[S_2O_8^{2-}]$ = 0.1 M and 35°C

μ	$[H^+]$, M	$[Tc(IV)]_0 \times 10^4$, M	k'_1, min^{-1}	$k'_2 \times 10^5$, mol l^{-1} min^{-1}	$k'_3 \times 10^5$, mol l^{-1} min^{-1}	k_1,* l mol^{-1} min^{-1}	k_3,** min^{-1}
1	0.25	1.7	0.080	1.10	450	0.80	113
1	0.5	1.7	0.085	2.15	250	0.85	125
1	0.5	1.7	0.080	2.15	260	0.80	130
1	0.75	1.7	0.090	3.20	160	0.90	120
1	1.00	1.7	0.090	4.30	100	0.90	100
1	1.00	5.2	0.080	4.30	120	0.80	120
1	1.00	3.5	0.095	4.30	110	0.95	110
		Average	0.086 ± 0.006			0.86 ± 0.06	117 ± 9
2	0.25	1.7	0.070	1.10	210	0.70	53
2	0.50	1.7	0.065	2.15	100	0.65	50
2	1.00	1.7	0.050	4.30	55	0.50	55
2	1.00	1.7	0.045	4.30	50	0.45	50
2	1.50	1.7	0.050	6.50	35	0.50	53
2	2.00	1.7	0.055	8.60	25	0.55	50
2	2.00	3.5	0.060	8.60	27	0.60	54
		Average	0.058 ± 0.008			0.58 ± 0.08	52 ± 2

* $k_1 = k'_1/[S_2O_8^{2-}]$. ** $k_3 = k'_3[H^+]$.

fortunately, because of the low accuracy of the rate constant determination (k'_1 and k'_2), especially at low temperatures (25 and 35°C), it is impossible to find the activation energies for the two reaction pathways separately. On the other hand, the overall reaction rates (W) found from the slopes of the initial portions of the kinetic curves [Tc(IV)]–time at various temperatures[3] are well described by the Arrhenius equation. These data at $[HClO_4]$ = 1 M, μ = 1, and $[S_2O_8^{2-}]$ = 0.1 M are as follows:

T, °C	$W \times 10^6$, mol l^{-1} min^{-1}
25	4.4
30	7.3
35	11.7
40	20.0

The activation energy of the overall reaction calculated from these data by the least-squares method is 77.7 ± 8.1 kJ mol^{-1}.

In the reaction studied, as in the other similar reactions, Tc(IV) acts, apparently, as a one-electron reductant and is oxidized to Tc(V), which then rapidly transforms into Tc(VII) by disproportionation or oxidation.[4] In this connection, it is appropriate to obtain independent data on the rate of the reaction between Tc(V) and $S_2O_8^{2-}$ ions. As mentioned above, since Tc(V) is unstable in $HClO_4$ solutions, we studied this reaction in HCl solutions.

It was shown by spectrophotometric titration at 290 nm (the absorption band of $TcOCl_5^{2-}$) that approximately 1 mol of Tc(V) is consumed in the reaction with 1 mol of $S_2O_8^{2-}$. Therefore, the stoichiometry of the reaction can be expressed by the equation

$$TcOCl_5^{2-} + S_2O_8^{2-} + 3H_2O = TcO_4^- + 2HSO_4^- + 4HCl + Cl^-. \quad (20)$$

Because of the high reaction rate even in HCl solution, the kinetic experiments were performed at $S_2O_8^{2-}$ concentrations by two orders of magnitude smaller than in the experiments with Tc(IV). It was found that reaction (20) obeys the second-order kinetic equation

$$-d[Tc(V)]/dt = k_4[Tc(V)][S_2O_8^{2-}], \quad (21)$$

where k_4 = 330 l mol^{-1} min^{-1} at [HCl] = 1 M and 24°C. At $[S_2O_8^{2-}]$ = 0.1 M, [HCl] = 1 M, and 25°C, Tc(V) completely transforms into Tc(VII) within approximately 10 s. Reaction (20) strongly decelerates with increasing the Cl^- concentration. Obviously, in the solutions free from Cl^- ions, i.e., in $HClO_4$ solutions, the Tc(V) oxidation under the conditions taken for the Tc(IV) reaction with $S_2O_8^{2-}$ is virtually instantaneous.

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[3] In the initial stage, up to 50–60% conversion, the dependence of [Tc(IV)] on time is approximately linear.

[4] Probably, Tc(VI) is also formed as intermediate; in accordance with [11], it disproportionates at a high rate in both acid and alkaline solutions.

The mechanism of the thermal decomposition of $S_2O_8^{2-}$ ions [reaction (7)], suggested in [9], is represented above.

As for the mechanism of the reaction between Tc(IV) and $S_2O_8^{2-}$ ions along the noncatalytic pathway, we can suggest that, in accordance with the experimental orders with respect to the reactants (first order) and H^+ ions (zero order), the limiting stage of this reaction pathway involves the charge transfer between the reactants existing in their main ionic forms TcO^{2+} and $S_2O_8^{2-}$, i.e.,

$$TcO^{2+} + S_2O_8^{2-} \rightarrow TcO^{3+} + SO_4^{2-} + SO_4^{\bullet-}. \qquad (22)$$

Equation (22) is represented assuming that Tc(IV) in solutions of noncomplexing acids exists as TcO^{2+} cation [12]. Peroxydisulfuric acid $H_2S_2O_8$ is a strong dibasic acid, and in solutions it exists in the form of the $S_2O_8^{2-}$ ions. For Tc(V) in $HClO_4$ solutions, the species TcO_3^-, TcO^{3+}, and TcO_2^+ are postulated [13, 14].

Similarly to [9, 10], fast stages of reduction of radical ions $SO_4^{\bullet-}$ formed in slow stage (22) can be represented as follows:

$$SO_4^{\bullet-} + H_2O \rightarrow HSO_4^- + OH, \qquad (23)$$

$$TcO^{2+} + OH \rightarrow TcO^{3+} + OH^-, \qquad (24)$$

$$H^+ + OH^- \rightarrow H_2O, \qquad (25)$$

$$TcO^{3+} + S_2O_8^{2-} + 3H_2O \rightarrow TcO_4^- + 2H_2SO_4 + 2H^+. \qquad (26)$$

Taking into account that, for the autocatalytic pathway, the reaction order with respect to H^+ ions is equal to –1, we can assume that in the limiting stage of this reaction pathway Tc(IV) reacts in the form of hydrolyzed ions $TcOOH^+$, whose concentration is inversely proportional to the concentration of H^+ ions. The second reactant, Caro acid, reacts in the slow stage of the reaction in the form of the HSO_5^- anion, since Caro acid dissociates as a monobasic acid [15].

Thus, the mechanism of the reaction between Tc(IV) and $S_2O_8^{2-}$ ions along the autocatalytic pathway can be represented as follows:

$$S_2O_8^{2-} + H^+ \rightarrow SO_4^{\bullet} + HSO_4^-, \qquad (4)$$

$$SO_4^{\bullet} + H_2O \rightarrow HSO_5^- + H^+, \qquad (27)$$

$$TcO^{2+} + H_2O \rightleftarrows TcOOH^+ + H^+, \qquad (28)$$

$$TcOOH^+ + HSO_5^- \rightarrow TcO_2^+ + SO_4^{\bullet-} + H_2O, \qquad (29)$$

$$TcO_2^+ + S_2O_8^{2-} + 2H_2O \rightarrow TcO_4^- + 2H_2SO_4, \qquad (30)$$

with stage (29) being the rate-determining stage, and the other stages being fast. The $SO_4^{\bullet-}$ radical ions are reduced in stages (23)–(26).

It should be noted that slow stages (22) and (29) involve reactions between ions of opposite charges, which agrees with the negative electrolytic effect observed.

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