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# Oxidation of U(IV) in $HNO_3$ Solutions Containing Urea and Tc(VII)

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**Abstract**—The kinetics of U(IV) oxidation with nitric acid in aqueous solutions containing urea, catalyzed with technetium ions, were studied by sampling with subsequent colorimetric determination of the U(IV) concentration. At the constant ionic strength of the solution $\mu = 2$ in the range of the initial concentrations of U(IV) from $2 \times 10^{-3}$ to $1.28 \times 10^{-2}$, Tc(VII) from $5 \times 10^{-5}$ to $1 \times 10^{-3}$, urea from 0.01 to 0.1, and hydrogen ions from 0.4 to 1.96 M, the reaction rate is described by the equation $-d[U(IV)]/dt = k_1[U(IV)][Tc]^{0.5}[CO(NH_2)_2] \times \{[H^+]^2 + \beta_1[H^+] + \beta_2\}^{-1} - k_2[U(IV)]^2[H^+]^{0.4}[CO(NH_2)_2]^{1.6}\{[H^+]^2 + \beta_1[H^+] + \beta_2\}^{-2}$, where $k_1 = 172 \pm 10$ mol$^{0.5}$ l$^{-0.5}$ min$^{-1}$ and $k_2 = (9.4 \pm 1.2) \times 10^2$ mol l$^{-1}$ min$^{-1}$ at 25°C, $\beta_1$ and $\beta_2$ are the hydrolysis constants of $U^{4+}$ ions. The activation energy is $63 \pm 2$ kJ mol$^{-1}$. A reaction mechanism is proposed, in which in the slow stages the complex ion $U(OH)_2^{2+} \cdot CO(NH_2)_2$ reacts with $TcO^{2+}$ and $TcO^{2+} \cdot CO(NH_2)_2$ ions.

Uranium(IV) is unstable in nitric acid solutions because of formation and accumulation of $HNO_2$, which is kinetically more effective oxidizing agent than $HNO_3$ [1]. To prevent U(IV) oxidation, a compound rapidly reacting with $HNO_2$, e.g., hydrazine, is added to the solution [2]. However, when solutions contain technetium ions, which catalyze the reaction between U(IV) and $HNO_3$ (nitrate ions), U(IV) is oxidized even in the presence of hydrazine [3]. Similar trends are also observed with another stabilizing agent for U(IV), hydroxylamine [4]. In this connection, it is of interest to study the catalytic effect of technetium ions with respect to U(IV) in solutions containing urea, which not only rapidly reacts with $HNO_2$ [5] but also forms a complex with U(IV).

This work is aimed to study the kinetics and mechanism of U(IV) oxidation in aqueous nitric acid solutions containing urea and technetium ions.

## EXPERIMENTAL

The procedure of kinetic experiments was as follows. Into a temperature-controlled 15-ml test tube, aliquots of stock solutions of all the components excluding U(IV) were added; the test tube was kept for 10 min to warm up to the required temperature. Then, a small aliquot of the stock solution of U(IV) (from 0.1 to 0.6 ml) was added, and aliquots of the working solution were withdrawn intermittently to determine the U(IV) concentration.

The concentration of U(IV) was determined colorimetrically with Arsenazo I. The optical measurements were carried out on a KFK-2-UKhL4.2 photocolorimeter with a red filter (wavelength 590 nm). In preliminary experiments it was found that, at pH ≤ 1.2, U(VI) (less than 10 g l$^{-1}$), urea, and Tc(VII) do not interfere with determination of U(IV) by this method.

## RESULTS AND DISCUSSION

The kinetic curves of U(IV) oxidation at the initial concentrations of Tc(VII) from $5 \times 10^{-5}$ to $1 \times 10^{-3}$ M are exponential for the most part. The kinetic curves are linearized in the coordinates ln[U(IV)]–time (Fig. 1), which corresponds to the first order with respect to U(IV). The apparent first-order rate constant ($k_a$) evaluated from the slope of the straight lines at $[CO(NH_2)_2] = 0.05$, $[H^+] = 1.5$ M, 25°C, and ionic

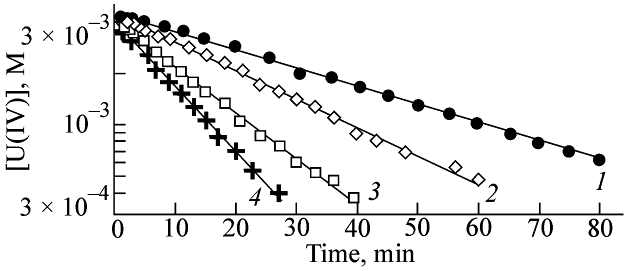

**Fig. 1.** Dependence of [U(IV)] on time at various initial concentrations of Tc(VII). $[H^+] = 1.5$, $[CO(NH_2)_2] = 0.05$ M, 25°C; $[Tc(VII)]_0$, M: (*1*) $5 \times 10^{-5}$, (*2*) $1 \times 10^{-4}$, (*3*) $2.5 \times 10^{-4}$, and (*4*) $5 \times 10^{-4}$.

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**Table 1.** Dependence of $k_a$ on the urea concentration at $[Tc(VII)] = 1 \times 10^{-4}$, $[U(IV)] = 4.25 \times 10^{-3}$, $[H^+] = 1$ M, 25°C, and $\mu = 2$

| $[CO(NH_2)_2]$, M | $k_a$, $min^{-1}$ | $k_2$,* $l^{1.5}\ mol^{-1.5}\ min^{-1}$ |
|---|---|---|
| 0.010 | 0.016 | 157 |
| 0.025 | 0.04 | 159 |
| 0.050 | 0.08 | 155 |
| 0.075 | 0.13 | 169 |
| 0.100 | 0.15 | 148 |
| | Average | 158 ± 8 |

* $k_2 = k_a/\{[CO(NH_2)_2)][Tc(VII)]^{0.5}\}$.

strength of the solution $\mu = 2$ increases in proportion to the square root of the Tc(VII) concentration:

| $[Tc(VII)] \times 10^4$, M | $k_a$, $min^{-1}$ | $[Tc(VII)] \times 10^4$, M | $k_a$, $min^{-1}$ |
|---|---|---|---|
| 0.5 | 0.025 | 5 | 0.091 |
| 1 | 0.039 | 7.5 | 0.104 |
| 2.5 | 0.061 | 10 | 0.127 |

The $k_a$ value decreases with increasing initial concentration of U(IV) in the range from $2.1 \times 10^{-3}$ to $1.28 \times 10^{-2}$ M according to Eq. (1)

$$k_a = k''_0 - k''_1[U(IV)]_0,\ min^{-1}, \qquad (1)$$

where $k''_0 = 0.096\ min^{-1}$ and $k''_1 = 3.84\ l\ mol^{-1}\ min^{-1}$ at 25°C and $\mu = 2$.

The dependence of the reaction rate on the urea concentration was studied in the range of $[CO(NH_2)_2]$ from 0.01 to 0.1 M at $[Tc(VII)] = 1 \times 10^{-4}$, $[U(IV)] = 4.2 \times 10^{-3}$, $[H^+] = 1$ M, 25°C, and $\mu = 2$. As seen from Table 1, $k_a$ values increase in direct proportion to $CO(NH_2)_2$ concentration and, hence, the reaction order with respect to urea is 1.

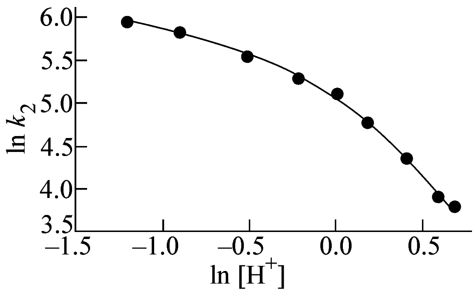

**Fig. 2.** Dependence of $\ln k_2$ on $\ln[H^+]$ at $[U(IV)] = 4.25 \times 10^{-3}$, $[Tc(VII)] = 1 \times 10^{-4}$, $[CO(NH_2)_2] = 0.05$ M, 25°C, and $\mu = 2$.

Thus, at a constant concentration of hydrogen ions, the rate of U(IV) oxidation is described by the equation

$$-d[U(IV)]/dt = (k'_0 - k'_1[U(IV)]_0)[U(IV)][Tc(VII)]^{0.5} \times [CO(NH_2)_2], \qquad (2)$$

where $k'_0 = 193\ l^{1.5}\ mol^{-1.5}\ min^{-1}$, $k'_1 = 7670\ l^{2.5}\ mol^{2.5}\ min^{-1}$ at $[H^+] = 1$ M, 25°C, and $\mu = 2$.

The influence of the concentration of hydrogen ions was studied in the range from 0.4 to 1.96 M at a constant ionic strength of the solution ($\mu = 2$) and 25°C. As seen from the data presented below ($[Tc(VII)] = 1 \times 10^{-4}$ and $[CO(NH_2)_2] = 0.05$ M), the rate of U(IV) oxidation decreases with increasing concentration of $H^+$ ions; in this case, the reaction order with respect to hydrogen ions decreases from –0.5 to –2 with increasing $[H^+]$ from 0.4 to 1.96 M (Fig. 2):

| $[H^+]$, M | $k_0$, $min^{-1}$ | $[H^+]$, M | $k_0$, $min^{-1}$ |
|---|---|---|---|
| 0.4 | 0.17 | 1.2 | 0.06 |
| 0.6 | 0.13 | 1.5 | 0.039 |
| 0.8 | 0.1 | 1.8 | 0.025 |
| 1 | 0.095 | 1.96 | 0.022 |

The influence of temperature on the reaction rate was studied in the range from 14.5 to 35.5°C at $[U(IV)] = 4.2 \times 10^{-3}$, $[Tc(VII)] = 1 \times 10^{-4}$, $[CO(NH_2)_2] = 0.05$, $[H^+] = 1$ M, and $\mu = 2$. From the values obtained (see below), the activation energy was determined to be $63 \pm 2$ kJ $mol^{-1}$.

| $T$, °C | $k_0$, $min^{-1}$ | $T$, °C | $k_0$, $min^{-1}$ |
|---|---|---|---|
| 14.5 | 0.03 | 30.5 | 0.12 |
| 20 | 0.05 | 35.5 | 0.18 |
| 25 | 0.08 | | |

Based on published data [6–10] on the reactions involving U(IV) and Tc(VII) in nitric acid solutions, the following scheme of U(IV) oxidation can be suggested:

$$3U^{4+} + 2TcO_4^- = 3UO_2^{2+} + 2TcO^{2+}, \qquad (3)$$

$$TcO_4^- + 2TcO^{2+} + 6H^+ \rightleftarrows 3TcO^{3+} + 3H_2O, \qquad (4)$$

$$3TcO^{3+} + 2HNO_3 + 5H_2O = 3TcO_4^- + 2NO + 10H^+, \qquad (5)$$

$$2NO + HNO_3 + H_2O \rightleftarrows 3HNO_2. \qquad (6)$$

It is readily seen that summation of these stages results in the stoichiometry of the overall reaction describing oxidation of U(IV) with $HNO_3$:

$$U^{4+} + HNO_3 + H_2O = UO_2^{2+} + HNO_2 + 2H^+. \quad (7)$$

In the suggested scheme, reactions (5) and (6) are considerably faster than reactions (3) and (4), which are rate-determining stages. In the presence of urea, nitrous acid formed is scavenged by the fast reaction

$$CO(NH_2)_2 + H^+ + HNO_2 = NH_4^+ + N_2 + H_2O + CO_2. \quad (8)$$

A high rate of this reaction is confirmed by the absence of peaks typical for $HNO_2$ in the absorption spectra of the working solutions.

It should also be noted that U(IV) can enter into reaction (3) not only in the form of $U^{4+}$ aqua ion, but also in the form of a complex with urea

$$3U^{4+}\cdot CO(NH_2)_2 + 2Tc(VII) = 3U(VI) + 2Tc(IV) + 3CO(NH_2)_2. \quad (9)$$

Thus, considering the rate-determining stages (3), (4), and (9), the expression for the rate of U(IV) oxidation can be written in the form

$$-d[U(IV)]/dt = k_1[U^{4+}][Tc(VII)] + k_2[U^{4+}\cdot CO(NH_2)_2][Tc(VII)] + k_3[Tc(IV)][Tc(VII)], \quad (10)$$

where $k_1$ and $k_2$ are the rate constants of oxidation of $U^{4+}$ aqua ion and complex ion $U^{4+}\cdot CO(NH_2)_2$ according to Eqs. (3) and (9), respectively, and $k_3$ is the rate constant of reaction (4). The concentrations of $U^{4+}$ and $U^{4+}\cdot CO(NH_2)_2$ can be found from the equation of mass balance for U(IV). Considering the constant of complex formation of U(IV) with urea $\alpha$

$$\alpha = [U^{4+}\cdot CO(NH_2)_2][U^{4+}]^{-1}[CO(NH_2)_2]^{-1}, \quad (11)$$

these concentrations are, respectively

$$[U^{4+}] = [U(IV)]\{1 + \alpha[CO(NH_2)_2]\}^{-1}, \quad (12)$$

$$[U^{4+}\cdot CO(NH_2)_2] = \frac{\alpha[U(IV)][CO(NH_2)_2]}{1 + \alpha[CO(NH_2)_2]}. \quad (13)$$

After substitution of Eqs. (12) and (13) in Eq. (10), we obtain

$$-d[U(IV)]/dt = k'[Tc(VII)][U(IV)] + k_3[Tc(IV)][Tc(VII)], \quad (14)$$

where

$$k' = \{k_1 + \alpha k_2[CO(NH_2)_2]\}\{1 + \alpha[CO(NH_2)_2]\}^{-1}. \quad (15)$$

To determine the concentrations of various valence forms of technetium, it is necessary to take into account that the rate of reaction (5) significantly exceeds the rate of reaction (4) and the equilibrium between two valence forms of technetium, Tc(VII) and Tc(IV), is established. Then, applying the steady state principle to Tc(IV) concentration, we can write

$$k'[U(IV)][Tc(VII)] = k_3[Tc(IV)][Tc(VII)]. \quad (16)$$

Taking into account the mass balance with respect to technetium, we obtain

$$[Tc(VII)] = [Tc] - k'[U(IV)]/k_3, \quad (17)$$

$$[Tc(IV)] = k'[U(IV)]/k_3, \quad (18)$$

where [Tc] is the total concentration of technetium in the solution. After substitution of Eqs. (17) and (18) in Eq. (14), we obtain (at constant concentrations of $H^+$ ions and urea)

$$-d[U(IV)]/dt = 2k'[Tc][U(IV)] - 2(k')^2[U(IV)]^2/k_3. \quad (19)$$

The results of the experimental study show that the reaction rate is described by the second-order equation with respect to uranium concentration:

$$-d[U(IV)]/dt = k_a[U(IV)]. \quad (20)$$

Equating the right sides of Eqs. (19) and (20), we obtain the expression for the apparent first-order rate constant

$$k_a = 2k'[Tc] - 2(k')^2[U(IV)]/k_3, \quad (21)$$

according to which $k_a$ is a linear function of U(IV) concentration. This conclusion is in good agreement with dependence (1) established experimentally at a constant acidity and constant Tc concentration. Equation (21) is also in good agreement with the fractional reaction order with respect to Tc, since in this equation the reaction rate by one of the pathways is independent of the Tc concentration, and that by the other pathway is in direct proportion to the Tc concentration.

Let us denote the initial concentration of tetravalent uranium, $[U(IV)]_0$, by $a$ and the change in the U(IV) concentration, by $x$. Then, Eq. (19) takes the form

$$-d(a - x)/dt = 2k'(a - x)[Tc] - 2(k')^2(a - x)^2/k_3. \quad (22)$$

**Table 2.** Dependence of rate constants $k'$ and $k_3$ on [U(IV)] at [Tc(VII)] = $1 \times 10^{-4}$, [H$^+$] = 1, [CO(NH$_2$)$_2$] = 0.05 M, 25°C, and $\mu$ = 2

| $[\mathrm{U(IV)}] \times 10^3$, M | $\frac{[\mathrm{CO(NH_2)_2}]}{[\mathrm{U(IV)}]}$ | $k'$ | $k_3 \times 10^{-6}$ |
|---|---|---|---|
| | | l mol$^{-1}$ min$^{-1}$ | |
| 2.13 | 23.4 | 450 | 0.135 |
| 4.18 | 12 | 500 | – |
| 4.25 | 11.7 | 445 | 0.132 |
| 6.38 | 7.83 | 430 | 0.082 |
| 8.52 | 5.86 | 410 | 0.084 |
| | Average | 447 ± 41 | 0.108 ± 0.03 |

After simple transformations of Eq. (22) and its subsequent integration, we obtain the equation

$$\ln\frac{a - x}{[\mathrm{Tc}] - k'(a - x)/k_3} = 2k'[\mathrm{Tc}]t + \ln\frac{a}{[\mathrm{Tc}] - k'a/k_3}, \quad (23)$$

presenting the linear function of its left side on time. The numerical values of the rate constants $k'$ and $k_3$ were found by selection of their ratio so that the correlation coefficient of the linear equation was no less than 0.9995. In the most cases, the influence of $k_3$ on linearization of the experimental data is insignificant and, therefore, the error in determination of $k_3$ is significantly greater than that in determination of $k'$. From the slope of the straight line, we found $k'$; and then $k_3$ was evaluated from the ratio $k'/k_3$. The rate constants $k'$ and $k_3$ found by the above procedure at various initial concentrations of U(IV) are listed in Table 2.

Table 2 shows that $k'$ and $k_3$ remain constant at a fairly high (more than approximately 6) ratio of the initial concentrations of urea and U(IV). At a lower value of this ratio, $k'$ decreases and $k_3$ increases. This is caused by the fact that, in solving Eq. (10), we assumed that the urea concentration remains constant in oxidation of U(IV). However, with increasing initial concentration of U(IV), the amount of HNO$_2$ formed increases; this HNO$_2$ reacts with urea by reaction (8) and decreases its concentration, and thus the urea concentration does not remain constant in the course of the reaction.

The rate constants $k'$ and $k_3$ evaluated by Eq. (23) using the experimental data at various CO(NH$_2$)$_2$ concentrations are listed in Table 3.

Based on data listed in Table 3, we plotted $k'$ vs. [CO(NH$_2$)$_2$]. This plot is a straight line. It can be readily shown that Eq. (15) obtained with the suggested mechanism transforms into a linear dependence on the urea concentration only in the case when the denominator is 1. Hence, $\alpha$ should be less than 1, and Eq. (15) thus takes the form

$$k' \approx k_1 + k_2\alpha[\mathrm{CO(NH_2)_2}]. \quad (24)$$

Since the straight line in the coordinates $k'$–[CO(NH$_2$)$_2$] passes practically through the origin, $k_1$ is close to 0 and, hence, the contribution of the reaction pathway involving U$^{4+}$ aqua ions to the total reaction rate can be neglected. Based on the above, the slow stage of the first reaction pathway is described by Eq. (9) and the expression for the reaction rate of this pathway is

$$-\mathrm{d}[\mathrm{U(IV)}]/\mathrm{d}t = k''[\mathrm{U(IV)}][\mathrm{Tc}][\mathrm{CO(NH_2)_2}], \quad (25)$$

where $k'' = \alpha k_2 = 9130 \pm 400$ l$^2$ mol$^{-2}$ min$^{-1}$ at [H$^+$] = 1 M, $\mu$ = 2, and 25°C. Since the complex formation constant $\alpha$ is unknown, $k_2$ in Eq. (24) cannot be evaluated, and in further discussion of the reaction mechanism we will use $k''$.

The reaction rate of the second slow stage, reproportionation of Tc(V), having the rate constant $k_3$, increases with urea concentration (Table 3). The reaction order with respect to urea, determined from data listed in Table 3, is 0.4, and, hence, the expression for

**Table 3.** Dependence of $k'$ and $k_3$ on urea concentration at [Tc(VII)] = $1 \times 10^{-4}$, [H$^+$] = 1 M, $\mu$ = 2, and 25°C

| [CO(NH$_2$)$_2$], M | $k'$ | $k_3 \times 10^4$ | $k''$,* l$^2$ mol$^{-2}$ min$^{-1}$ | $k'_3 \times 10^{-5}$,** l$^{1.4}$ mol$^{-1.4}$ min$^{-1}$ |
|---|---|---|---|---|
| | l mol$^{-1}$ min$^{-1}$ | | | |
| 0.0095 | 83 | 2.3 | 8700 | 1.48 |
| 0.025 | 230 | 3.5 | 9200 | 1.53 |
| 0.05 | 447 | 4.5 | 8940 | 1.49 |
| 0.075 | 750 | 5.4 | 9330 | 1.52 |
| 0.1 | 950 | 6.0 | 9500 | 1.51 |
| | | Average | 9130 ± 400 | 1.51 ± 0.03 |

* $k'' = k'/[\mathrm{CO(NH_2)_2}]$. ** $k'_3 = k_3/[\mathrm{CO(NH_2)_2}]^{0.4}$.

**Table 4.** Dependence of $k'$ and $k_3$ on the concentration of $H^+$ ions at [Tc(VII)] = $1 \times 10^{-4}$, $[CO(NH_2)_2]$ = 0.05 M, $\mu$ = 2, and 25°C

| $[H^+]$, M | $k'$, $l\ mol^{-1}\ min^{-1}$ | $k''$, $l^2\ mol^{-2}\ min^{-1}$ | $k_6$,* $min^{-1}$ | $k_3 \times 10^{-4}$, $l\ mol^{-1}\ min^{-1}$ | $k'_3 \times 10^{-5}$, $l^{1.4}\ mol^{-1.4}\ min^{-1}$ | $k_7$** $\times 10^{-5}$, $l\ mol^{-1}\ min^{-1}$ |
|---|---|---|---|---|---|---|
| 0.4 | 1125 | 22 500 | (3880) | 6.66 | 2.21 | 1.53 |
| 0.6 | 900 | 18 000 | (6820) | 5.78 | 1.91 | 1.56 |
| 0.8 | 625 | 12 500 | 8310 | 5.58 | 1.85 | 1.69 |
| 1 | 450 | 9130 | 9280 | 4.54 | 1.51 | 1.51 |
| 1.2 | 300 | 6000 | 8860 | – | – | – |
| 1.5 | 185 | 3700 | 8500 | – | – | – |
| 1.8 | 135 | 2700 | 8900 | – | – | – |
| 1.96 | 100 | 2000 | 7800 | – | – | – |
| | | Average | 8610 ± 520 | | Average | 1.57 ± 0.08 |

* $k_6 = k''([H^+]^2 + \beta_1[H^+] + \beta_2)$. ** $k_7 = k'_3[H^+]^{0.4}$.

the reaction rate by pathway (4) can be written in the form

$$-d[U(IV)]/dt = k'_3[Tc[IV)][Tc(VII)][CO(NH_2)_2]^{0.4}, \quad (26)$$

where $k'_3 = (1.51 \pm 0.03) \times 10^5\ l^{1.4}\ mol^{-1.4}\ min^{-1}$ at $[H^+]$ = 1 M, $\mu$ = 2, and 25°C.

The dependence of $k_3$ on the urea concentration can be understood assuming that Tc(IV) enters into the reaction with Tc(VII) along Eq. (4) not only in the form of the $TcO^{2+}$ ion but also in the form of a complex ion containing urea:

$$2TcO^{2+} \cdot CO(NH_2)_2 + TcO_4^- \rightarrow 3TcO^{3+} + 2CO(NH_2)_2. \quad (27)$$

The constant of formation of this complex $\alpha_3$

$$TcO^{2+} + CO(NH_2)_2 \rightleftarrows TcO^{2+} \cdot CO(NH_2)_2 \quad (28)$$

is equal to

$$\alpha_3 = [TcO^{2+} \cdot CO(NH_2)_2][TcO^{2+}]^{-1}[CO(NH_3)_2]^{-1}. \quad (29)$$

In this case, the equation for the rate of U(IV) consumption along the second pathway can be written in the form

$$-d[U(IV)]/dt = k_4[TcO^{2+}][Tc(VII)] + k_5[TcO^{2+} \cdot CO(NH_2)_2][Tc(VII)]. \quad (30)$$

From the equation of the mass balance for Tc(IV), we can find the concentrations of $TcO^{2+}$ and $TcO^{2+} \cdot CO(NH_2)_2$ ions. Substituting these concentrations in Eq. (30), we obtain

$$-\frac{d[U(IV)]}{dt} = \frac{k_4 + k_5\alpha_3[CO(NH_2)_2]}{1 + \alpha_3[CO(NH_2)_2]}[Tc(IV)][Tc(VII)]. \quad (31)$$

Equating the right side of Eq. (31) to the second term of Eq. (14), we obtain the equation

$$k_3 = \{k_4 + k_5\alpha_3[CO(NH_2)_2]\}\{1 + \alpha_3[CO(NH_2)_2]\}^{-1}. \quad (32)$$

Using data listed in Table 3 and Eq. (32), we estimated graphically the rate constants $k_4$ and $k_5$ in Eq. (29) and constants of complex formation ($\alpha_3$) of urea with Tc(IV) to be 16 200 $l\ mol^{-1}\ min^{-1}$, $1.1 \times 10^5\ l^2\ mol^{-2}\ min^{-1}$, and 9 $l\ mol^{-1}$, respectively, at 25°C.

To determine the dependence of the rate constants $k'$ and $k_3$ on the concentration of hydrogen ions, the experimental data were processed by Eq. (21). The results are listed in Table 4 (the $k_3$ values at $[H^+] >$ 1 M are not given because of poor accuracy in their determination). The dependence plotted in the coordinates $\ln k''$–$\ln[H^+]$ using these data (Fig. 3) is linear in the range of concentration of hydrogen ions from 0.8 to 1.96 M with the slope equal to –2 (at $[H^+] <$ 0.8 M, the dependence deviates from linearity).

The resulting dependence can be rationalized by assuming that U(IV) enters into reaction (9) with Tc(VII) in the form of hydrolyzed ion $U(OH)_2^{2+} \cdot CO(NH_2)_2$, as suggested in [10]. Then, the expression

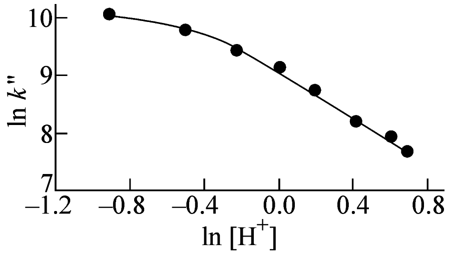

**Fig. 3.** Dependence of $\ln k'$ on $\ln[H^+]$. [Tc(VII)] = $1 \times 10^{-4}$, $[CO(NH_2)_2]$ = 0.05 M, $\mu$ = 2, and 25°C.

for the rate of this reaction pathway can by presented by the equation

$$-\mathrm{d[U(IV)]/d}t = \chi[\mathrm{U(OH)_2^{2+}\cdot CO(NH_2)_2}][\mathrm{Tc(VII)}]. \quad (33)$$

Considering the mass balance with respect to U(IV),

$$[\mathrm{U(IV)}] = [\mathrm{U^{4+}}] + [\mathrm{UOH^{3+}}] + [\mathrm{U(OH)_2^{2+}}] + [\mathrm{U(OH)_2^{2+}\cdot CO(NH_2)_2}], \quad (34)$$

the expression for the concentration of this ion can be written in the form

$$[\mathrm{U(OH)_2^{2+}\cdot CO(NH_2)_2}] = \frac{[\mathrm{U(IV)}]\,\beta_2\alpha_2\,[\mathrm{CO(NH_2)_2}]}{[\mathrm{H^+}]^2 + \beta_1[\mathrm{H^+}] + \beta_2 + \beta_2\alpha_2[\mathrm{CO(NH_2)_2}]}, \quad (35)$$

where $\beta_1$ and $\beta_2$ are the constants of the first and the second stages of U(IV) hydrolysis, and $\alpha_2$ is the equilibrium constant of formation of the complex $\mathrm{U(OH)_2^{2+}\cdot CO(NH_2)_2}$.

The term $\beta_2\alpha_2[\mathrm{CO(NH_2)_2}]$ in the denominator of Eq. (35) can be neglected because of its small value in comparison with the other terms, and then, after substitution of Eq. (35) in Eq. (33), we obtain

$$-\frac{\mathrm{d[U(IV)]}}{\mathrm{d}t} = \frac{\chi[\mathrm{U(IV)}]\,\beta_2\alpha_2\,[\mathrm{CO(NH_2)_2}][\mathrm{Tc(VII)}]}{[\mathrm{H^+}]^2 + \beta_1[\mathrm{H^+}] + \beta_2}. \quad (36)$$

Comparison of Eqs. (34) and (23) shows that

$$k'' = k_6\{[\mathrm{H^+}]^2 + \beta_1[\mathrm{H^+}] + \beta_2\}^{-1}, \quad (37)$$

where $k_6 = \alpha_2\beta_2\chi$. Expression (37) adequately describes the dependence of $k''$ on the concentration of hydrogen ions in the range from 0.8 to 2 M at the hydrolysis constants $\beta_1 = 0.031$ and $\beta_2 = 1 \times 10^{-4}$ M [11].

Considering Eq. (37), the rate of the second reaction pathway [Eq. (9)] can be described by the expression

$$-\frac{\mathrm{d[U(IV)]}}{\mathrm{d}t} = \frac{k_6[\mathrm{U(IV)}][\mathrm{Tc}][\mathrm{CO(NH_2)_2}]}{[\mathrm{H^+}]^2 + \beta_1[\mathrm{H^+}] + \beta_2}, \quad (38)$$

in which $k_6 = 8610 \pm 520$ min$^{-1}$ at $[\mathrm{H^+}] = 0.8$–2.0, $[\mathrm{Tc(VII)}] = 1 \times 10^{-4}$ M, $\mu = 2$, and 25°C.

The dependence of the rate constant $k_3'$ on the concentration of hydrogen ions is presented in Table 4. These data show that the reaction order with respect to $\mathrm{H^+}$ ions for the second pathway is $-0.4$ in the range of $[\mathrm{H^+}]$ from 0.4 to 1 M.

Thus, the total kinetic equation for oxidation of U(IV) obtained using the suggested reaction mechanism is

$$\begin{aligned}-\mathrm{d[U(IV)]/d}t &= k_8[\mathrm{U(IV)}][\mathrm{Tc}]^{0.5}[\mathrm{CO(NH_2)_2}] \\ &\times\{[\mathrm{H^+}]^2 + \beta_1[\mathrm{H^+}] + \beta_2\}^{-1} \\ &- k_9[\mathrm{U(IV)}]^2[\mathrm{H^+}]^{0.4}[\mathrm{CO(NH_2)_2}]^{1.6}\{[\mathrm{H^+}]^2 + \beta_1[\mathrm{H^+}] + \beta_2\}^{-2},\end{aligned} \quad (39)$$

where $k_8 = 2k_6/[\mathrm{Tc}]^{0.5} = 172 \pm 10$ mol$^{0.5}$ l$^{-0.5}$ min$^{-1}$ and $k_9 = 2(k_6)^2/k_7 = (9.4 \pm 1.2) \times 10^2$ mol l$^{-1}$ min$^{-1}$ at 25°C and ionic strength equal to 2.

Comparison of Eq. (39) with kinetic equation (18) established experimentally shows that the apparent first-order constant $k_\mathrm{a}$ is

$$\begin{aligned}k_\mathrm{a} &= k_8[\mathrm{Tc}]^{0.5}[\mathrm{CO(NH_2)_2}]\{[\mathrm{H^+}]^2 + \beta_1[\mathrm{H^+}] + \beta_2\}^{-1} \\ &- k_9[\mathrm{U(IV)}][\mathrm{H^+}]^{0.4}[\mathrm{CO(NH_2)_2}]^{1.6}\{[\mathrm{H^+}]^2 + \beta_1[\mathrm{H^+}] + \beta_2\}^{-2}.\end{aligned} \quad (40)$$

The $k_\mathrm{a}$ evaluated from this equation agrees within ±12% with the values found experimentally under all the studied conditions except the runs at low concentrations of $\mathrm{H^+}$ ions (less than 0.4 M), where the discrepancy exceeds 50%.

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