An unusually intense effect of the medium acidity on the rate of oxidation of U^{4+} and the yield of chemiluminescence in aqueous solutions of $HClO_4$ containing $K_2S_2O_8$

L. A. Khamidullina,* S. V. Lotnik, and V. P. Kazakov

Institute of Organic Chemistry, Ufa Scientific Center of the Russian Academy of Sciences,
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: 007 (347 2) 35 6066. E-mail: kazakov@chemlum.bashkiria.su

Light emission from aqueous solutions of $HClO_4$ containing U^{4+} and $S_2O_8{}^{2-}$ has been observed. The emitter of chemiluminescence (CL) is the electron-excited uranyl ion ($^*UO_2{}^{2+}$), the product of U^{4+} oxidation. A hundredfold decrease in the $HClO_4$ concentration (from 1 to 0.01 mol L^{-1}) results in a 250-fold increase in the reaction rate constant, a 5000-fold increase in the initial CL (from $4 \cdot 10^5$ to $2 \cdot 10^9$ photon s^{-1}), a more than tenfold increase in the CL yield (from $5.6 \cdot 10^{-8}$ to $1.6 \cdot 10^{-6}$), and a 200-fold increase in the excitation yield of $UO_2{}^{2+}$ (from $6 \cdot 10^{-6}$ to $1.3 \cdot 10^{-3}$). The kinetic isotope effect of the reaction has been studied. The value for the ratio of the rate constants $k_H/k_D = 2.1$ has been determined by extrapolation to the 100% degree of deuteration of 0.1 *M* perchloric acid. The peculiarities of the chemiluminescence stage in the reaction of U^{4+} oxidation in solutions of potassium persulfate were explained by the participation of the products of hydrolysis of the U^{4+} aqua ion (UOH^{3+} and $U(OH)_2{}^{2+}$), whose relative fraction increases as the $HClO_4$ concentration decreases.

Key words: uranium(IV), uranyl ion ($UO_2{}^{2+}$), persulfate ion, chemiluminescence, kinetic isotope effect.

About thirty reactions of oxidation of tetravalence uranium have been studied up to date;[1] however, the light emission was observed only for the reactions of U^{4+} and some oxygen-containing oxidants, such as O_3, OF_2,[2] H_2O_2,[3] XeO_3,[4–6] and XeF_2.[7] The study of reactions accompanied by chemiluminescence (CL) provides an additional opportunity to refine the mechanism resulting in the formation of the uranyl ion in the electron-excited state ($UO_2{}^{2+}$). In this work, we established that the oxidation of U^{4+} in acidic aqueous solutions of potassium persulfate is accompanied by CL and revealed the unusually strong effect of pH of the medium on the rate of the chemiluminescence stage of the reaction and parameters of CL, such as the chemiluminescence yield (η_{CL}) and the yield of excitation of the light emitter (η_{ex}).

Experimental

CL was studied on a photometric setup, which detects light beams with intensity greater than $1.5 \cdot 10^4$ photon s^{-1} in the blue spectral region. An FEU-140 photoelectron multiplier was used as the detector (spectral region of the photocathode sensitivity 200—650 nm). The reagents used ($K_2S_2O_8$, $UO_2(ClO_4)_2$, and $HClO_4$) were additionally purified. Uranium(IV) perchlorate was obtained by the electrolytic reduction of uranyl perchlorate in 1 *M* $HClO_4$ on a Pt cathode. The solutions studied (10 mL) were prepared prior to each experiment by dilution of solutions of $K_2S_2O_8$ (10^{-2} mol L^{-1}) in 1 *M* $HClO_4$ and $U(ClO_4)_4$ (10^{-2} mol L^{-1}) in 1 *M* $HClO_4$ with bidistilled water and/or a 1 *M* solution of $HClO_4$ and poured into thermostatted (with accuracy of ±0.1 °C) Pyrex or Teflon (F-4D) reaction vessels 40 mm in diameter. Distilled D_2O (Izotop plant, A grade, degree of deuteration 99.0—99.9%, specific electroconductivity at 298 K $1 \cdot 10^{-6}$ Ohm^{-1} cm^{-1}) was used for deuteration of the solvent.

When solutions of U^{4+} and $K_2S_2O_8$ in 0.01—1 *M* $HClO_4$ are mixed, light emission is observed, whose intensity depends substantially on the pH of the medium. Using glass light filters with a sharp transmission boundary, we established that the spectral regions of the observed CL coincide with those of the photoluminescence of perchloric solutions of the uranyl ion. Therefore, electron-excited $^*UO_2{}^{2+}$, the product of oxidation of U^{4+}, is the emitter of CL.

Results and Discussion

The dark stage of the reaction is known[8,9] to be caused by the interaction between U^{4+} and $S_2O_8{}^{2-}$; however, we do not rule out that the products of hydrolysis of persulfate ($HSO_5{}^-$, H_2O_2, and $SO_4{}^{2-}$) can contribute noticeably to the chemiluminescence stage. The kinetics of CL was studied with a 10—100-fold excess of $K_2S_2O_8$, assuming that the chemiluminescence stage of oxidation of U^{4+} in solutions of potassium persulfate, as the dark stage,[8,9] has first order with respect to each of the reagents:

$$-d[U^{4+}]/dt = k \cdot [U^{4+}] \cdot [S_2O_8{}^{2-}]. \quad (1)$$

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 12, pp. 2134—2139, December, 1997.

The overall concentration of the oxidant was assumed equal to the concentration of $S_2O_8^{2-}$. Under these conditions

$$I = \eta_{CL}k[U^{4+}] = \eta_{CL}k[U^{4+}]_0 \cdot \exp(-kt), \qquad (2)$$

$$\log I = \lg\eta_{CL}k[U^{4+}]_0 - 0.4343kt, \qquad (3)$$

where $k = k_0[S_2O_8^{2-}]_0$, and η_{CL} is the CL yield.

The first-order rate constant k and then the bimolecular constant k_0 were determined from the tangent slope of the linear region of the time dependence of the logarithm of the CL intensity (I) (Fig. 1, curves *1*—*6*). The temperature dependence of the rate constant of the chemiluminescence stage of the oxidation of U^{4+} in 1 M $HClO_4$ obeys the Arrhenius equation (Fig. 1, curves *7* and *8*). The activation energy of the reaction (E_a) in 1 M $HClO_4$ in the 278—313 K temperature range is equal to 72±5 kJ mol^{-1}. Curves *7* and *8* have no break in the region of 303 K, unlike the dependence of ln$K$ on $1/T$ obtained for the oxidation of U^{4+} by the persulfate ion in 1.92 M $HClO_4$.[9] This means that the mechanism of the chemiluminescence stage of the reaction undergoes no substantial changes in the temperature range from 278 to 313 K. The k_0 values at the same temperature are almost independent of the initial concentration of U^{4+} ($[U^{4+}]_0$) when it is changed tenfold from 10^{-4} to 10^{-5} mol L^{-1} (see Fig. 1, curves *7* and *8*, respectively). The reaction has first order with respect to U^{4+}, which is also retained in the range $10^{-6} \le [U^{4+}]_0 \le 10^{-5}$ mol L^{-1} and in 0.1 M $HClO_4$ (Fig. 2, curves *1*—*4*). Some decrease in k_0 is observed only at lower values of the concentration of U^{4+}. The dependences of the initial CL intensity (I_0) and light sum (S) on the concentration of U^{4+} in the solution are satisfactorily rectified in double logarithmic coordinates (see Fig. 2). Curves *7* and *8* are almost parallel to each other, *i.e.*, I_0 and S are related proportionally. Both these plots can be used as calibration for the determination of the concentration of U^{4+} in the range of 10^{-7}—$6 \cdot 10^{-5}$ mol L^{-1} of U^{4+} at $[S_2O_8^{2-}]_0 = 10^{-4}$ mol L^{-1}. When $[S_2O_8^{2-}]_0$ increases to 10^{-3} mol L^{-1}, the range of U^{4+} concentrations increases to 10^{-8}—10^{-4} mol L^{-1}. Using solutions of $K_2S_2O_8$, the detection limit of U^{4+} can be decreased by at least one more order of magnitude by increasing the concentration of the oxidant and decreasing pH of the solution; however, the analytical possibilities of this chemiluminescence reaction are exceeded by a system using xenon trioxide as the oxidant.[5,6]

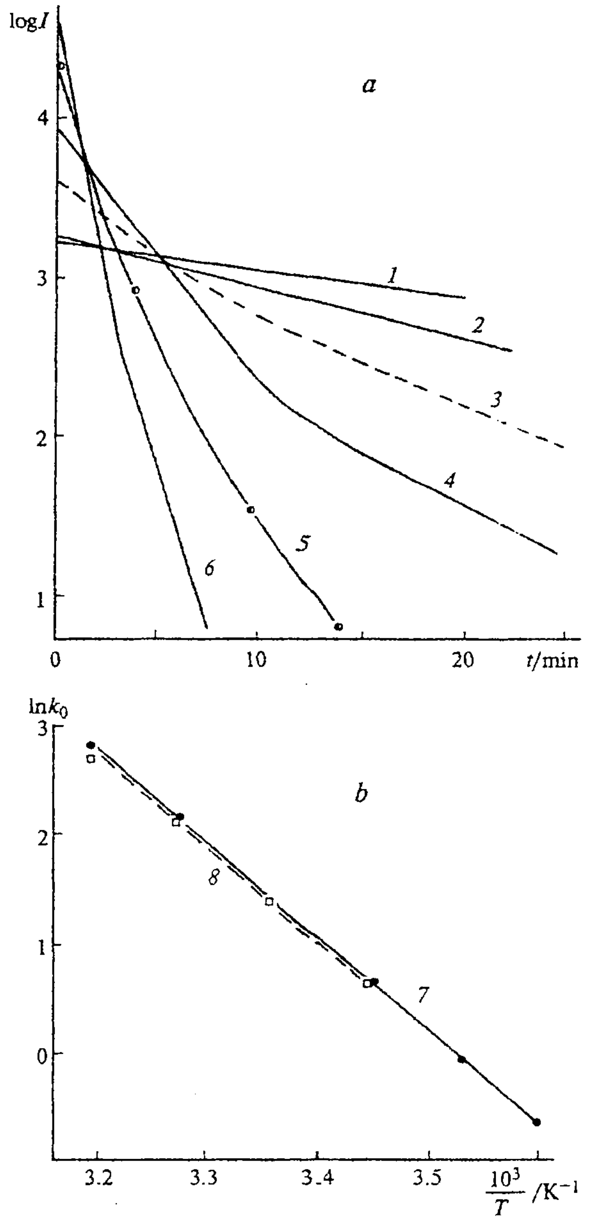


Fig. 1. *a*. Time dependence of the intensity of chemiluminescence accompanying the U^{4+} oxidation in a solution of potassium persulfate at the temperature (T/K): 278 (*1*), 283 (*2*), 290 (*3*), 298 (*4*), 305 (*5*), and 310 (*6*). *b*. Temperature dependence of the bimolecular rate constant of the chemiluminescence stage of the reaction in the Arrhenius coordinates (*7*, *8*): $[HClO_4] = 1$ mol L^{-1}; $[U^{4+}]_0 = 10^{-4}$ mol L^{-1}; $[S_2O_8^{2-}] = 10^{-3}$ mol L^{-1} (*7*); $[U^{4+}] = 10^{-5}$ mol L^{-1}; and $[S_2O_8^{2-}] = 10^{-4}$ mol L^{-1} (*8*).

The intensity of CL and the rate of the U^{4+} oxidation depend strongly on the concentration of $HClO_4$. The high sensitivity of the chemiluminescence method, which allows one to detect beams different in intensity by several orders of magnitude, gave data on the reaction kinetics and CL parameters when the concentration of the acid changed from 1 mol L^{-1} to 0.01 mol L^{-1} with the concentrations of U^{4+} (10^{-5} mol L^{-1}) and $S_2O_8^{2-}$ (10^{-4} mol L^{-1}) remaining unchanged. For many redox reactions involving U^{4+}, the kinetic equation of type (1) is fulfilled[1] when the degree of conversion is not greater than 60—80%. The kinetic curves contain the exponential regions covering the change in the CL intensity by three orders of magnitude (Fig. 3, curves *1*—*3*), which correspond approximately to a thousandfold decrease in the concentration of U^{4+} (this follows

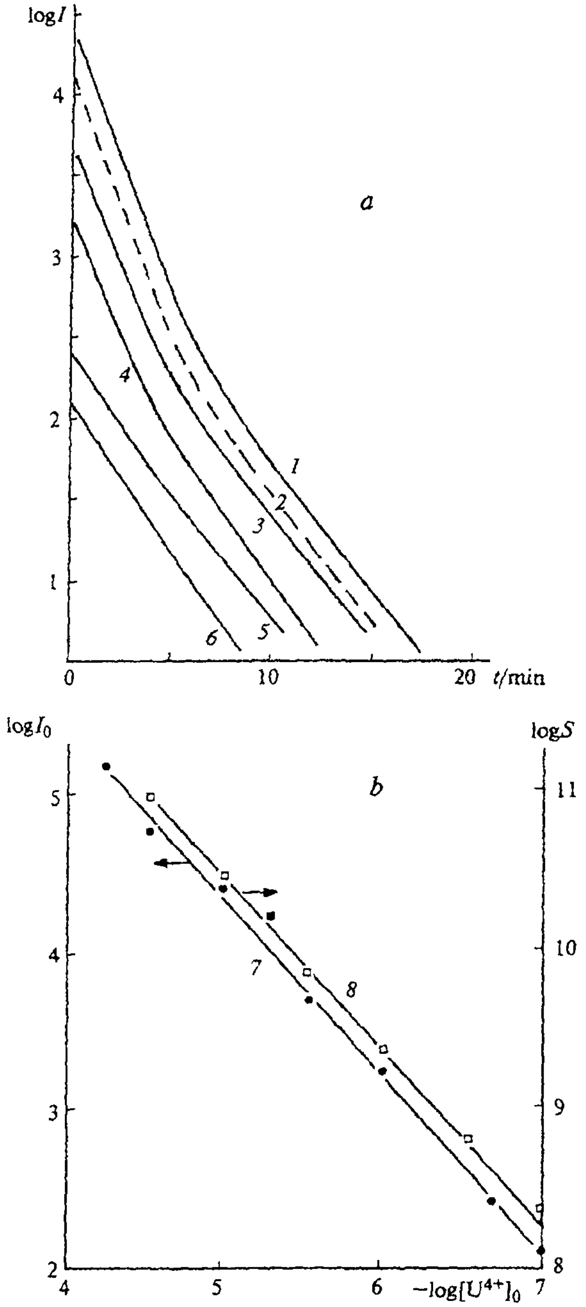


Fig. 2. *a*. Curves of the chemiluminescence decay in a solution of $K_2S_2O_8$ at $[U^{4+}]$/mol L^{-1}: $1 \cdot 10^{-5}$ (*1*), $5 \cdot 10^{-6}$ (*2*), $3 \cdot 10^{-6}$ (*3*), $1 \cdot 10^{-6}$ (*4*), $2 \cdot 10^{-7}$ (*5*), and $1 \cdot 10^{-7}$ (*6*). *b*. Dependences of the initial chemiluminescence intensity (I_0) (*7*) and its light sum (*S*) (*8*) on the concentration of U^{4+} in the solution in double logarithmic coordinates. T = 298 K; $[HClO_4]$ = 0.1 mol L^{-1}; $[S_2O_8{}^{2-}] = 10^{-4}$ mol L^{-1}.

from the data shown in Fig. 2). This indicates that a reaction first order with respect to uranium is retained up to the degree of conversion >99.9%.

In the concentration range of 1—0.3 mol L^{-1} $HClO_4$, the initial CL intensity and the rate constant k_0 increase exponentially (Fig. 3, curves *10* and *11*). When the pH of the medium increases, the increase in I_0 and k_0 is no

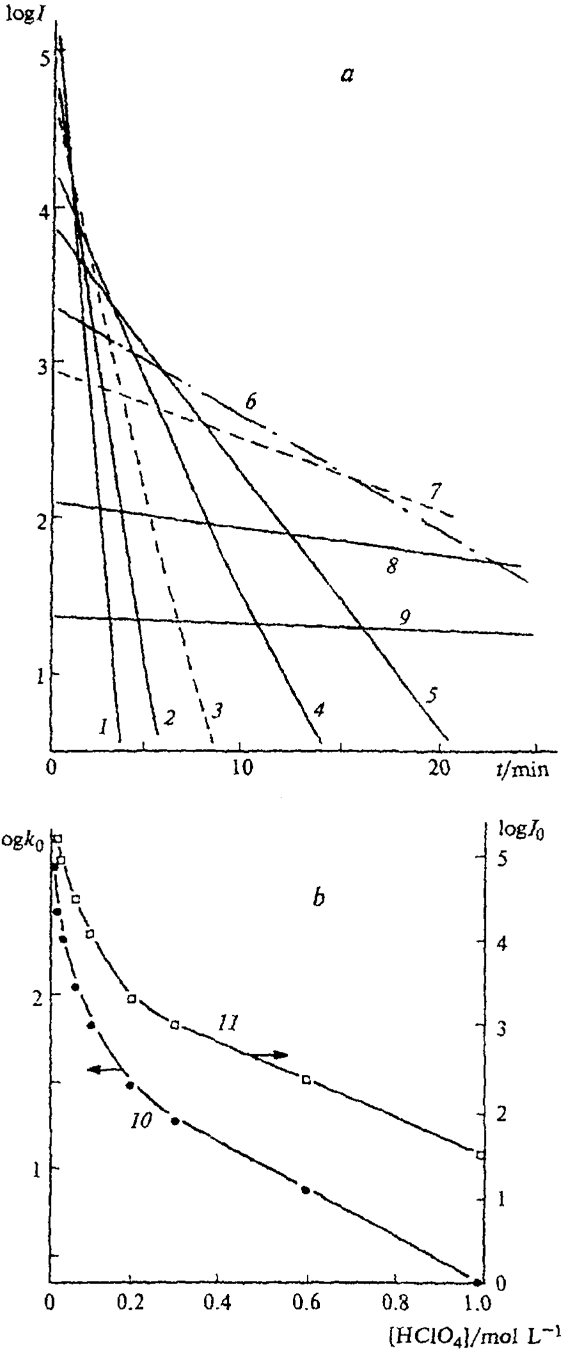


Fig. 3. *a*. Kinetics of chemiluminescence in the reaction of U^{4+} and $S_2O_8{}^{2-}$ in aqueous solutions of $HClO_4$ at $[HClO_4]$/mol L^{-1}: 0.01 (*1*), 0.02 (*2*), 0.03 (*3*), 0.06 (*4*), 0.1 (*5*), 0.2 (*6*), 0.3 (*7*), 0.6 (*8*), and 1.0 (*9*). *b*. Semilogarithmic anamorphoses of the dependences of the rate constant (k_0) (*10*) and initial chemiluminescence intensity (I_0) (*11*) on the concentration of $HClO_4$. $[U^{4+}]_0 = 10^{-5}$ mol L^{-1}; $[S_2O_8{}^{2-}] = 10^{-4}$ mol L^{-1}; T = 291.5 K.

Table 1. Values of the initial chemiluminescence intensity (I_0), rate constant (k_0) of the chemiluminescence stage of the U^{4+} oxidation in a solution of $K_2S_2O_8$, light sum (S), lifetime (τ), yields of chemiluminescence (η_{CL}), radiation of the $^*UO_2^{2+}$ emitter (η_{em}), excitation of the chemiluminescence emitter (η_{ex}) at different concentrations of [$HClO_4$] in the solution

[$HClO_4$] /mol L^{-1}	log(I_0/photon s^{-1})	k_0 /mol L^{-1} s^{-1}	log$S$	$\eta_{CL} \cdot 10^8$	$\tau_{UO_2^{2+}}$ /μs	$\eta_{em} \cdot 10^3$	$\eta_{ex} \cdot 10^5$
1.0	5.6	2.1	9.5	5.6	6.8	9	0.6
0.6	6.3	5.5	9.65	7.9	4.8	6.3	1.3
0.3	7.2	16	9.9	13	3.4	4.5	2.9
0.2	7.6	28	10.1	21	2.8	3.7	5.7
0.1	8.1	62	10.3	32	2.4	3.2	10.2
0.06	8.5	100	10.45	47	1.8	2.4	19.6
0.03	8.8	200	10.6	63	1.4	1.8	35
0.02	9	280	10.75	89	1.2	1.6	56
0.01	9.3	520	11	165	1	1.3	127

Note. T = 291.5 K, $[U^{4+}]_0 = 10^{-5}$ mol L^{-1}, $[S_2O_8^{2-}] = 10^{-4}$ mol L^{-1}.

longer described by exponentials. The dependence of k_0 on the concentration of $HClO_4$ in the range 0.01 mol $L^{-1} \le [HClO_4] \le 0.1$ mol L^{-1} is satisfactorily rectified in the coordinates logk_0—log[$HClO_4$] (Fig. 4, curve *1*). When the concentration of $HClO_4$ changes by two orders of magnitude (from 1 to 0.01 mol L^{-1}), k_0 increases by 250 times (from 2.1 to 520 L mol^{-1} s^{-1}), I_0 increases by 5000 times (from $4 \cdot 10^5$ to $2 \cdot 10^9$ photon s^{-1}), and S increases by 14 times (Table 1).

The almost 30-fold increase in the CL yield (η_{CL}) determined as the ratio of the number of emitted photons to the number of molecules of the light emitter (Fig. 4, curve *2*) is also of interest. One could expect a decrease in the η_{CL} values on going to more dilute (in acid) solution, since it is known that the emission yield (η_{em}) of $^*UO_2^{2+}$ decreases noticeably. The lifetime of the uranyl ion in the electron-excited state (τ) at T = 298 K in 1 M $HClO_4$ is equal[10] to 6.8 μs, and in 0.01 M $HClO_4$ it is 1 μs. The η_{em} value at the temperature T can be determined from the lifetime of the uranyl ion at this temperature (τ_T) and 77 K ($\tau_{77\ K}$): $\eta_{em} = \tau_T/\tau_{77\ K}$. The emission yield at 77 K is close to unity.

The τ values presented in Table 1 were obtained by interpolation: τ = 6.8 μs for 1 M $HClO_4$, 1 μs for 0.01 M $HClO_4$,[10] and 2.2—2.4 μs for 0.1 M $HClO_4$[11,12]. For 0.4 M $HClO_4$ at 300 K, $\eta_{em} = 4.2 \cdot 10^{-3}$.[2] Determining the $\tau_{77\ K}$ value from the latter and taking into account that it remains almost unchanged in frozen solutions of $HClO_4$ (1—0.01 M), we calculated the emission yields of $^*UO_2^{2+}$ at different concentrations of $HClO_4$. The η_{em} values thus determined change sevenfold (from $9 \cdot 10^{-3}$ to $1.3 \cdot 10^{-3}$) when [$HClO_4$] decreases from 1 to

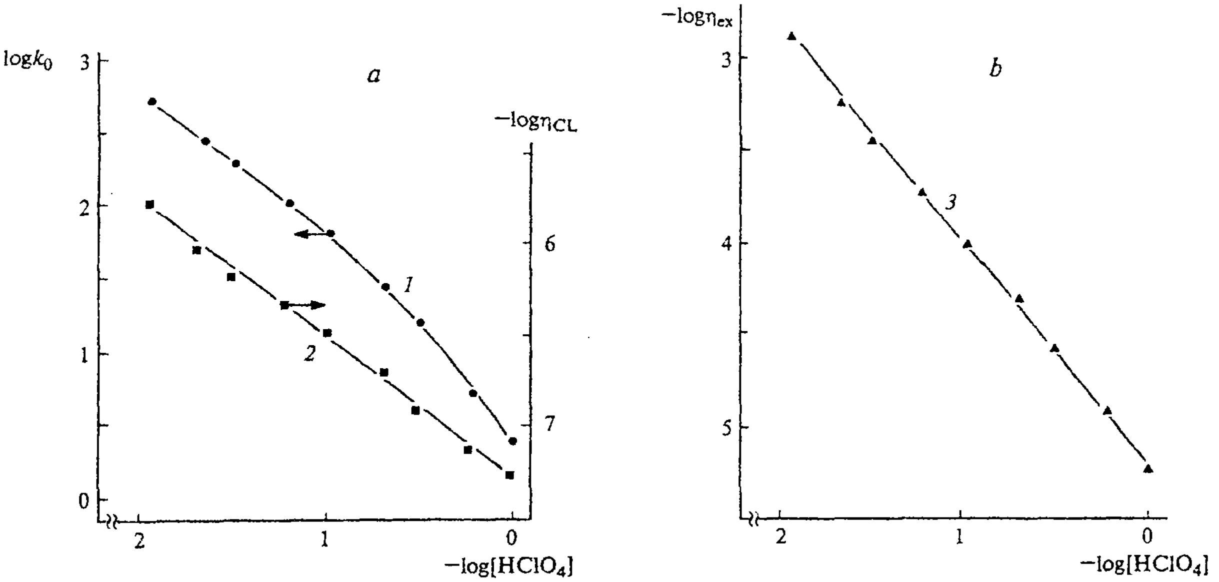


Fig. 4. *a*. Dependences of the rate constant of the chemiluminescence stage of the oxidation of U^{4+} by potassium persulfate (k_0) (*1*) and chemiluminescence yield (η_{CL}) (*2*) on the $HClO_4$ concentration in the solution in double logarithmic coordinates. *b*. Dependences of the excitation yield of UO_2^{2-} (η_{ex}) (*3*) on the $HClO_4$ concentration in the solution in double logarithmic coordinates. $[U^{4+}]_0 = 10^{-5}$ mol L^{-1}; $[S_2O_8^{2-}] = 10^{-4}$ mol L^{-1}; T = 291.5 K.

0.01 mol L^{-1}. The value of the excitation yield of the emitter (η_{ex}), which is related to η_{CL} and η_{em} by the correlation $\eta_{CL} = \eta_{ex} \cdot \eta_{em}$, increases by 210 times (from $6 \cdot 10^{-6}$ to $1.3 \cdot 10^{-3}$) when the acidity of the solution decreases in the range studied (1—0.01 mol L^{-1}) (Fig. 4, curve *3* and Table 1).

The more than 200-fold increase in the k_0 rate constant and η_{ex}, as the concentration of $HClO_4$ decreases from 1 to 0.01 mol L^{-1}, can be explained by the participation of several forms of U^{4+} in the chemiluminescence process. In 1 *M* $HClO_4$, almost all tetravalent uranium is present in the solution as the U^{4+} aqua ion, while when the pH of the medium increases, the hydrolysis reaction occurs:

$$U^{4+} + H_2O \overset{K}{\rightleftharpoons} UOH^{3+} + H^+. \quad (4)$$

Knowing the equilibrium constant K = 0.0258 mol L^{-1}, it is easy to calculate[13] that in 0.1 *M* $HClO_4$ 21% U^{4+} is present in the form of UOH^{3+}, and in 0.05 *M* $HClO_4$, 34%. The following redox reactions occur in 1 *M* $HClO_4$:

$$2\,U^{4+} + S_2O_8^{2-} + 4\,H_2O \longrightarrow 2\,UO_2^{+} + 2\,HSO_4^{-} + 6\,H^+, \quad (5)$$

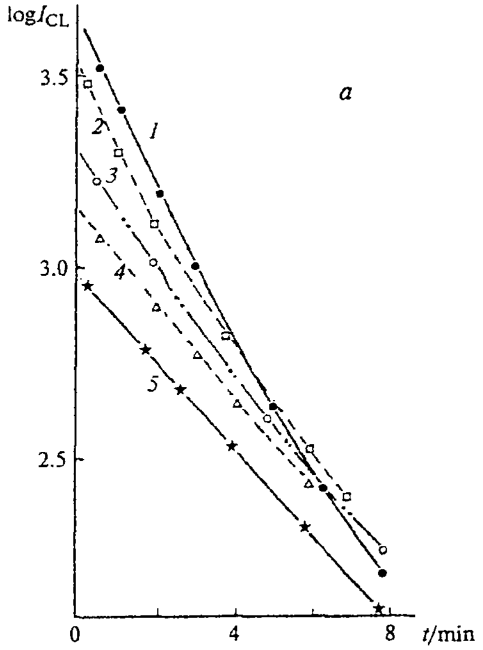
$$UO_2^{+} + S_2O_8^{2-} \longrightarrow UO_2^{2+} + SO_4^{\cdot -} + SO_4^{2-}, \quad (6)$$

$$U^{4+} + SO_4^{\cdot -} + 2\,H_2O \longrightarrow UO_2^{+} + HSO_4^{-} + 3\,H^+, \quad (7)$$

$$UO_2^{+} + SO_4^{\cdot -} \longrightarrow UO_2^{2+} + SO_4^{2-}. \quad (8)$$

We believe that the interaction between U^{4+} and $S_2O_8^{2-}$ includes the intermediate formation of the pentavalent uranium salt (UO_2^{+}), whose subsequent oxidation is an elementary act of the chemiluminescence stage of the reaction. The participation of Caro's acid and H_2O_2, formed in the hydrolysis of persulfate and HSO_5^{-}, respectively,[14] in the oxidation of U^{4+} cannot be ruled out; however, further studies are required to determine their contribution to the CL observed.

The increase in the oxidation rate of U^{4+}, when solutions with a lower concentration of $HClO_4$ are used, can be explained by the fact that hydroxo forms of U^{4+} participate in the redox process. The monotonic increase in η_{CL} and η_{ex} (Fig. 4, curves *2* and *3*, respectively) indicate that the formation of excited $^*UO_2^{2+}$ occurs more efficiently when UOH^{3+} is present in the solution.



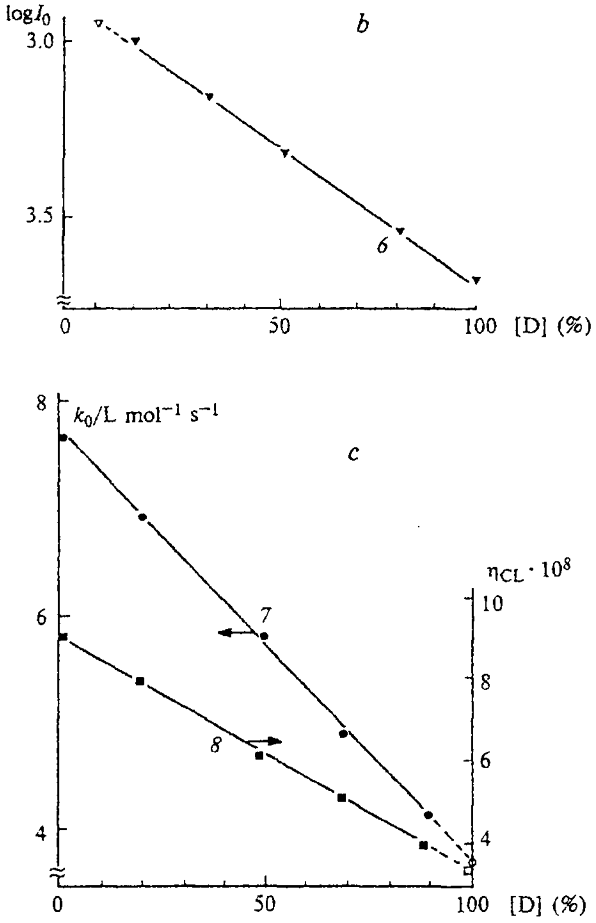


Fig. 5. *a*. Semilogarithmic anamorphoses of the decay of chemiluminescence appeared in the reaction of U^{4+} and $S_2O_8^{2-}$ in a solution of 0.1 *M* $HClO_4$ with the content of deuterium (%): 0 (*1*), 20 (*2*), 50 (*3*), 70 (*4*), and 90 (*5*). *b*. Dependence of the initial chemiluminescence intensity on the degree of deuteration of the solvent (*6*). *c*. Dependences of the reaction rate constant (k_0) (*7*) and chemiluminescence yield (η_{CL}) (*8*) on the degree of deuteration of the solvent. [$HClO_4$] = 0.1 mol L^{-1}; $[U^{4+}]_0 = 10^{-5}$ mol L^{-1}; $[S_2O_8^{2-}] = 10^{-3}$ mol L^{-1}; T = 298 K.

The participation of hydrogen-containing species in the reaction studied is supported by the observed kinetic isotope effect (KIE). The time dependences of the CL intensity at different concentrations of deuterium in the solution are shown in Fig. 5 (curves *1—5*). An increase in the degree of deuteration is accompanied by the exponential decrease in I_0 (curve *6*) and the linear decrease in k_0 and η_{CL} (curves *7* and *8*). Extrapolation of the dependence of k_0 on [D] to a 100% content of deuterium in the solution gave the value of KIE $k_{\mathrm{H}}/k_{\mathrm{D}}$ = 2.1 in 0.1 *M* $HClO_4$. The similar extrapolation of curves *6* and *8* (see Fig. 5) gave the values of the initial CL intensity $I_{0\,(\mathrm{D})}$ and CL yield ($\eta_{\mathrm{CL}\,(\mathrm{D})}$) at 100% substitution of hydrogen by deuterium: $I_{0\,(\mathrm{H})}/I_{0\,(\mathrm{D})} = 5.3$, $\eta_{\mathrm{CL}\,(\mathrm{H})}/\eta_{\mathrm{CL}\,(\mathrm{D})} = 9 \cdot 10^{-8}/3.5 \cdot 10^{-8} = 2.6$. According to expression (5), I_0 is proportional to $\eta_{\mathrm{CL}} \cdot k_0$; therefore, $I_{0\,(\mathrm{H})}/I_{0\,(\mathrm{D})} = \eta_{\mathrm{CL}\,(\mathrm{H})} \cdot k_{\mathrm{H}}/\eta_{\mathrm{CL}\,(\mathrm{D})} \cdot k_{\mathrm{D}}$. In fact, inserting the values of $\eta_{\mathrm{CL}\,(\mathrm{H})}$, $\eta_{\mathrm{CL}\,(\mathrm{D})}$, and KIE ($k_{\mathrm{H}}/k_{\mathrm{D}}$) in this expression, we have $2.6 \cdot 2.1 = 5.4$, which coincides within the overall measurement error (20%) with the value of the $I_{0\,(\mathrm{H})}/I_{0\,(\mathrm{D})}$ ratio. The result obtained testifies that the I value during the whole reaction reflects the rate of consumption of U^{4+}.

The monotonic decrease in η_{CL} as the degree of isotope substitution increases means a decrease in the excitation yield of the uranyl ion in the oxidation of UOD^{3+} in a solution of potassium persulfate, since it is known that in deuterated solutions η_{em} of $^*UO_2{}^{2+}$ is higher than in nondeuterated solutions.[15] A solvent has a noticeable effect on chemical reaction rates only in the case where the hydrogen atoms of the reagents participate in exchange with the solvent or when the latter reacts with dissolved polar compounds.[16] We believe that the oxidation reaction with the participation of hydroxo forms of U^{4+} includes the elimination of the hydrogen or deuterium atom from UOH^{3+} or UOD^{3+} ($U(OH)_2{}^{2+}$ or $U(OD)_2{}^{2+}$ at high pH values).

The existence of one, the more so two, oxygen atoms bound to the U^{4+} atom makes the process of formation of $UO_2{}^+$ ion more efficient than the oxidation of the U^{4+} aqua ion. This may be the reason for the acceleration of the oxidation of U^{4+} in solutions containing $S_2O_8{}^{2-}$ as the concentration of $HClO_4$ decreases.

References

1. V. S. Koltunov, *Kinetika reaktsii aktinoidov* [*Kinetics of Actinide Reactions*], Atomizdat, Moscow, 1974, 312 pp. (in Russian).
2. V. P. Kazakov, *Khemilyuminestsentsiya uranila, lantanoidov, i d-elementov* [*Chemiluminescence of Uranyl, Lanthanides, and d-Elements*], Nauka, Moscow, 1980, 176 pp. (in Russian).
3. A. K. Shtol'ts, V. K. Slepukhin, and Yu. A. Kovyazin, *Tr. Ural'sk. Pedagog. In-ta* [*Proc. Ural Pedagogical Inst.*], 1971, **189**, 20 (in Russian).
4. V. P. Kazakov, Yu. K. Gusev, G. S. Parshin, and L. A. Khamidullina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 2634 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1977, **26** (Engl. Transl.)].
5. L. A. Khamidullina, S. V. Lotnik, and V. P. Kazakov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 751 [*Russ. Chem. Bull.*, 1994, **43**, 704 (Engl. Transl.)].
6. S. V. Lotnik, L. A. Khamidullina, and V. P. Kazakov, *Kinet. Katal.*, 1995, **36**, 198 [*Kinet. Catal.*, 1995, **36** (Engl. Transl.)].
7. S. V. Lotnik and V. P. Kazakov, *Nizkotemperaturnaya khemilyuminestsentsiya* [*Low-Temperature Chemiluminescence*], Nauka, Moscow, 1987, 176 pp. (in Russian).
8. E. A. Kanevskii and L. A. Fedorova, *Radiokhimiya*, 1960, **2**, 559 [*Sov. Radiochem.*, 1960, **2** (Engl. Transl.)].
9. V. A. Ermakov, *Radiokhimiya*, 1985, **27**, 726 [*Sov. Radiochem.*, 1985, **27** (Engl. Transl.)].
10. M. Moriasu, Yu. Yokoama, and S. Ikeda, *J. Inorg. Nucl. Chem.*, 1977, **39**, 2211.
11. R. Matsushima and S. Sakuraba, *J. Am. Chem. Soc.*, 1971, **93**, 5421.
12. S. S. Ostakhov, V. P. Kazakov, D. D. Afonichev, and V. V. Rykova, *Radiokhimiya*, 1995, **37**, 503 [*Radiochem.*, 1995, **37** (Engl. Transl.)].
13. A. K. Pikaev, V. P. Shilov, and V. I. Spitsyn, *Radioliz vodnykh rastvorov lantanoidov i aktinidov* [*Radiolysis of Aqueous Solutions of Lanthanides and Actinides*], Nauka, Moscow, 1983, 240 pp. (in Russian).
14. I. M. Kolthoff and I. K. Miller, *J. Am. Chem. Soc.*, 1951, **73**, 3055.
15. H. D. Burrows and T. J. Kemp, *Chem. Soc. Rev.*, 1974, **3**, 139.
16. L. Melander and W. H. Saunders, Jr., *Reaction Rates of Isotopic Molecules*, John Wiley and Sons, New York, 1980.

Received May 30, 1997