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Chemiluminescence of Tb(IV) Reduction in Solution and Sensitization thereof with UO_2^{2+} Ions

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Abstract

Chemiluminescence was observed in Tb^{4+} reduction with water, the $\overset{*}{T}b^{3+}$ ions being the emitters. The polyphosphorotungstate (PW) anions were shown to stabilize the tetravalent state of terbium by being effective quenchers of the Tb^{3+} electron excited ions. This is the reason for the absence of chemiluminescence in the reductions of [Tb(IV)·PW] complexes with a number of reducing agents. The kinetics of the Tb^{4+} reduction with water after rapid dilution of the solution was studied by chemiluminescence, spectrophotometry and kinetic luminescence spectroscopy methods. The quenching of the Tb^{3+} photoluminescence with Tb^{4+} ions was shown to occur by electron transfer. It was proved that the chemiluminescence intensity increased more than one order with the introduction of UO_2^{2+} ions, the luminescence of which was uneffected by the PW anions. The addition of uranyl ions into the solution resulted in desactivation of the Tb^{3+} ions by electron excitation energy transfer to the uranyl ions.

Introduction

It is well known that in aqueous solutions some lanthanides can be involved in redox reactions. Thus, Ce^{3+} ions are readily converted into Ce^{4+}, and those of Eu^{3+}, Sm^{3+} and Yb^{3+} may be reduced to their divalent states. Higher stabilities are inherent to the divalent lanthanides in non-aqueous solutions [1], particularly in crystalline matrices [2]. In the latter, thermoluminescence occurs with the formation of excited lanthanide ions, which are considered to be the result of redox transformations [3–5].

It is known that high yields of excited states are often realized in those chemical reactions where the main elemental excitation is represented by electron transfer with bond breaks and bond formations, provided that the shifts of the molecule and atom species are negligible during excitation. These conditions are met in bright chemiluminescence reactions of dioxethane degradation and annihilation of the aromatic anion- and cation-radicals. A chemiluminescence reaction with electron transfer and with the molecular geometry virtually unchanged is observed in reductions (electron solvated ones as well) of tris(bipyridine)ruthenium(III) complexes.

$$Ru^{3+} + e^- \longrightarrow \overset{*}{R}u^{2+};\quad \overset{*}{R}u^{2+} \longrightarrow Ru^{2+} + h\nu \qquad (1)$$

Therefore, this confirms the formation of excited ions of lanthanides in the course of their redox transformations in solution. Of particular interest is the lanthanide chemiluminescence in reductions of tetravalent ions. The high energy gain in these reactions leads us to suggest that there is no other way for the electron transfer to the Ln^{4+} ion other than via the excited levels of the f-shell of the trivalent ion formed, since the electron-vibrating interactions of the ion coordination spheres and the f-electrons are rather weak in the latter and may result in desactivation with sphere changes in the course of the reaction. In other words, the specific nature of the lanthanide f-shell attracts our attention to the problem of energy dissipation on thermal vibrations followed by electron transfer to the Ln^{4+} ion, provided that the electron appears in the f-shell sublevels.

Experimental

A glass thermostated vessel containing the reaction mixture was put in a light-proof box on the photocathode of an FEU-39 photoelectron multiplier, the signals of which were recorded on an EPPV-60 potentiometer. The FEU was equipped with a VS-22 stabilized power supply. Light absorption of the solution was registered on a Specord M40 device. Photoluminescence spectra were recorded on an MPF-4 Hitachi fluorimeter. All compounds were chemically pure and PFA grade reactants. All solutions were prepared in double distilled water. The vessel was thermostated at 298 K.

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Results and Discussion

With the electrolysis of acidic solutions, our attempts to discover any luminous radiation out of the near-cathode space which could be explained by the equation $\mathrm{Eu^{3+} + e^- \rightarrow \overset{*}{Eu}{}^{2+}}$ failed, probably because of desactivation of the $\mathrm{\overset{*}{Eu}{}^{2+}}$ excited ions through chemical interactions with the solvent [6, 7]. By analogy with reaction (1), chemiluminescence should be expected on reduction of the lanthanide tetravalent ions:

$$\mathrm{Ln^{4+} + e^- \longrightarrow \overset{*}{Ln}{}^{3+};\quad \overset{*}{Ln}{}^{3+} \longrightarrow Ln^{3+}} + h\nu \qquad (2)$$

The authors of refs. 8–10 reported the production of aqueous solutions of tetravalent terbium and praseodymium assisted by the tungsten phosphoric acid anions $[\mathrm{P_2W_{11}O_{39}{\cdot}H_2O}]^{7-}$ and $[\mathrm{P_2W_{17}O_{61}{\cdot}H_2O}]^{10-}$. We reproduced the results reported and found the behaviour of $\mathrm{Tb^{4+}}$ and $\mathrm{Pr^{4+}}$ to correspond completely to that described. However, our attempts to observe any chemiluminescence during $\mathrm{Tb^{4+}}$ reduction in such solutions with hydrogen peroxide, sodium sulfite and other reducing agents failed. The reductions proceed very fast; e.g. in the reagent concentration region of 10^{-4} M the reactions were over in 1–2 s.

We were the first to describe the formation of $\mathrm{\overset{*}{Tb}{}^{3+}}$ excited ions during reduction from the tetravalent state [11, 12]. With concentrations of 10^{-4} M for Tb and Pr, and 4×10^{-4} M for polyphosphorotungstate, the tetravalent ions of those elements remain stable in 0.1 M $\mathrm{H_2SO_4}$ solution. Chemiluminescence was observed with that solution half diluted with 0.1 M $\mathrm{H_2SO_4}$ solution. In this case, the complexes dissociate to allow water to reduce the lanthanide ions:

$$\mathrm{Tb^{4+} + H_2O} \begin{array}{l} \nearrow \mathrm{\overset{*}{Tb}{}^{3+}} \\ \searrow \mathrm{Tb^{3+} + OH^{\bullet} + H^+} \end{array}$$

$$\mathrm{Pr^{4+} + H_2O} \begin{array}{l} \nearrow \mathrm{Pr^{3+} + OH^{\bullet} + H^+} \\ \searrow \mathrm{\overset{*}{Pr}{}^{3+}} \end{array} \qquad (3)$$

According to refs. 9 and 10, $\mathrm{Tb^{3+}}$ is quantiatively transformed into its tetravalent state in the process of potassium persulfate oxidation in a solution of potassium polyphosphorotungstate heated to 50 °C.

We found $\mathrm{Tb^{4+}}$ was formed in $\mathrm{K_{10}P_2W_{17}O_{61}}$–$\mathrm{K_2S_2O_8}$ solution without heating but with UV irradiation. Two ways are possible for the $\mathrm{Tb^{3+}}$ to $\mathrm{Tb^{4+}}$ transformation: the first one is via $\mathrm{Tb^{3+}}$ ion excitation followed by its oxidation wiht the $\mathrm{S_2O_8{}^{2-}}$ ion; and the second one consists of the photochemical decay of $\mathrm{S_2O_8{}^{2-}}$ with formation of $\mathrm{SO_4^{\bullet -}}$ ion radicals and further oxidation of the $\mathrm{Tb^{3+}}$ ion.

$$\mathrm{Tb^{3+}} + h\nu \longrightarrow \mathrm{\overset{*}{Tb}{}^{3+}}$$

$$\mathrm{\overset{*}{Tb}{}^{3+} + S_2O_8{}^{2-} \longrightarrow Tb^{4+} + SO_4{}^{2-} + SO_4^{\bullet -}} \qquad (4)$$

$$\mathrm{S_2O_8{}^{2-}} + h\nu \longrightarrow \mathrm{2SO_4^{\bullet -}};$$

$$\mathrm{Tb^{3+} + SO_4^{\bullet -} \longrightarrow Tb^{4+} + SO_4{}^{2-}} \qquad (5)$$

The former way suggests an effective desactivation of $\mathrm{\overset{*}{Tb}{}^{3+}}$ with the $\mathrm{S_2O_8{}^{2-}}$ ion. However, studies into the quenching of the $\mathrm{Tb^{3+}}$ ion fluorescence by potassium persulfate did not prove that eqn. (4) would take place. Along with the well-known photochemical reaction of $\mathrm{S_2O_8{}^{2-}}$ decay to radicals, the absence of quenching with persulfate ions makes the reaction of eqn. (5) preferable.

The ions of $\mathrm{P_2W_{17}O_{61}{}^{10-}}$ appeared to be effective enough in quenching the $\mathrm{\overset{*}{Tb}{}^{3+}}$ fluorescence (Fig. 1). In this case, the $\mathrm{Tb^{3+}}$ concentration was much higher than that of the $\mathrm{P_2W_{17}O_{61}{}^{10-}}$ ions, therefore only a small amount of $\mathrm{Tb^{3+}}$ would exist in the form of the $[\mathrm{Tb^{3+}{\cdot}P_2W_{17}{\cdot}O_{61}{}^{10-}}]$ complex. Thus, the quenching constant derived in the low concentration region of the complexing agent may refer to the process of production of the complex possessing the bimolecular constant k_b.

$$\mathrm{\overset{*}{Tb}{}^{3+} + [P_2W_{17}O_{61}{}^{10-}]} \xrightarrow{k_\mathrm{b}} [\mathrm{Tb^{3+}{\cdot}P_2W_{17}O_{61}{}^{10-}}] \qquad (6)$$

From the equation $I_0/I - 1 = k_\mathrm{b}\tau_0[\mathrm{P_2W_{17}O_{61}{}^{10-}}]$ and being aware of the lifetimes of the $\mathrm{Tb^{3+}}$ ions in their excited states, $\tau_0 = 4 \times 10^{-4}$ s (in the low concentration region of the quencher), we found $k_\mathrm{b} = 4 \times 10^{6}\ \mathrm{l\ mol^{-1}\ s^{-1}}$.

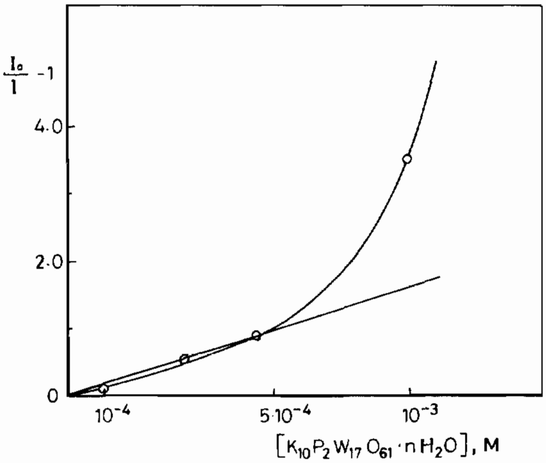

Fig. 1. Dependence of the quenching of the photoluminescence of the $\mathrm{Tb^{3+}}$ ions by polyphosphorotungstate ions in 0.1 M $\mathrm{H_2SO_4}$ solution according to the Stern–Volmer law. $[\mathrm{Tb^{3+}}] = 3 \times 10^{-3}$ M, $T = 298$ K.

With a high concentration of the quencher, the deviations from the Stern–Volmer law are conditioned by an increase in the Tb^{3+} portion bonded in a strong complex. The complexing equilibrium constant was not precisely determined for the Tb^{3+} ions, however, it is quite similar to the Ce^{3+} ions [13]. Since the equilibrium constants (k_e) for the lanthanides are usually of similar values, from the known values of k_e and k_b we may easily derive a rate constant for the complex dissociation (k_d) by putting $k_e = k_b/k_d$.

$$Tb^{3+} + [P_2W_{17}O_{61}{}^{10-}] \underset{k_d}{\xrightarrow{k_b}} [Tb^{3+}\cdot P_2W_{17}O_{61}{}^{10-}] \quad (7)$$

In accordance with ref. 13, the equilibrium constant value (k_e) for $Ce(P_2W_{17}O_{61})_2{}^{17-}$ is *ca.* 5×10^{17} mol^{2-}. Hence, the k_d value is rather small. If we assume k_e for the first stage to be six orders lower than the complete constant, the calculations of k_d result in a very low value, which is at least a few orders lower than the rate constant of the irradiation desactivation. Of course, the values mentioned depend on the extent to which the equilibrium constants are correct (eqn. 7), and the rate constant of the reaction with the excited Tb^{3+} ions ($k_b{}^*$) approximates to that of the ground state. Unfortunately, there was not any evidence for the correlation of the rate constants in the latter case, despite some progress using the kinetic spectroscopy method to investigate the kinetics of changes in the lanthanide coordination spheres [14]. However, the rate constants should be expected to possess similar values since the excited f-shell would hardly exert an important influence on the lanthanide coordination bonding where the f-shell is not involved.

It should be noted that $\overset{*}{Tb}{}^{3+}$ is desactivated by polyphosphorotungstate ions in fluid solutions only, while in frozen ones (77 K) the Tb^{3+} complexes produce bright fluorescence [15]. It is quite evident that it is the effective desactivation of the excited $\overset{*}{Tb}{}^{3+}$ ions by $P_2W_{17}O_{61}{}^{10-}$, those forming the coordination sphere, that causes the absence of chemiluminescence in reductions of $[Tb^{4+}\cdot(P_2W_{17}O_{61}{}^{10-})_2]$ complexes by a series of reducing agents. If the Tb^{3+} ions in that complex are formed in their excited states in the course of the reduction: $[Tb(P_2W_{17}O_{61})_2]^{16-}$ + reducing agent $\rightarrow$ $[Tb(P_2W_{17}O_{61})_2{}^*]^{17-} \rightsquigarrow [Tb(P_2W_{17}O_{61})_2]^{17-}$, they should be desactivated completely, since during the lifetime of the excited $\overset{*}{Tb}{}^{3+}$ ions ($\sim 10^{-4}$ s) they are not able to leave the coordination environment of the polyphosphorotungstate anions (according to the complex dissociation constant).

The observation of emission of the excited $\overset{*}{Tb}{}^{3+}$ ions formed in the Tb^{4+} reduction becomes possible in the case of the rapid dilution of the Tb^{4+} solution stabilized by $P_2W_{17}O_{61}{}^{10-}$ to such an anion concentration where a certain portion of the $\overset{*}{Tb}{}^{3+}$ ions can still avoid desactivation. The dilution is followed by a decrease in both the chemiluminescence intensity and the solution optical density with time, with the Tb^{4+} absorption band being assigned to the curve consisting of two components (Fig. 2).

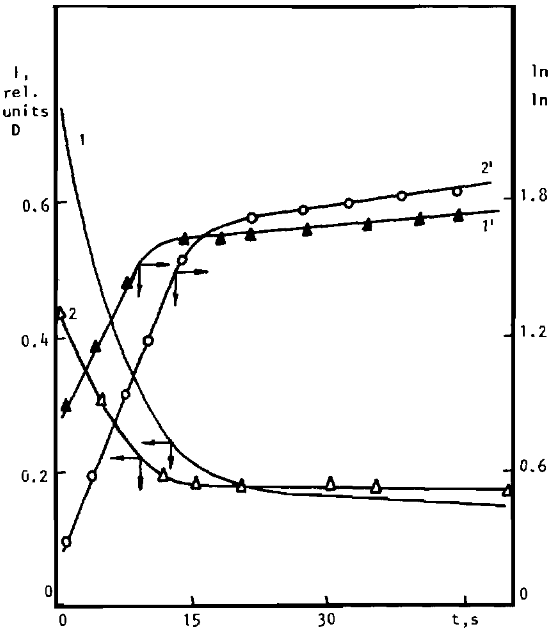

Fig. 2. The dependence with time of the chemiluminescence intensity in the reduction of Tb^{4+} ions with water molecules (1.1′) and the optical density of the solution (2.2′) with $\lambda = 430$ nm ($l = 5$ cm). The curves were plotted as result of the rapid ten-fold dilution with 0.1 M H_2SO_4 for the initial solution containing $[Tb^{4+}] = 10^{-3}$ M, $[K_{10}P_2W_{17}O_{61}] = 4 \times 10^{-3}$ M in 0.1 M H_2SO_4, $T = 298$ K.

The chemiluminescence spectral region determined with the boundary filters gives us evidence to assume Tb^{3+} to be the emitter. Besides, the chemiluminescence intensity increases in D_2O, being conditioned by the higher emission yield of Tb^{3+} ions in heavy water [16].

In the initial solution, before dilution, the Tb^{4+} ion exists in the form of complexes which dissociate step-by-step following the dilution.

$$\begin{aligned}&[Tb^{4+}\cdot(P_2W_{17}O_{61}{}^{10-})_2] \xrightarrow{k'_d} \\ &\qquad [Tb^{4+}\cdot P_2W_{17}O_{61}{}^{10-}] + P_2W_{17}O_{61}{}^{10-} \\ &[Tb^{4+}\cdot P_2W_{17}O_{61}{}^{10-}] \xrightarrow{k_d} Tb^{4+} + P_2W_{17}O_{61}{}^{10-}\end{aligned} \quad (9)$$

The limiting stages of the chemiluminescence kinetics are probably represented by the dissociation stages described above, while the reduction of free Tb^{4+} is a rapid process. The two sections of the kinetic curves both for the chemiluminescence and the optical density cannot be explained by the two stages of complex dissociation, since the excitation occurs at the rapid stage which immediately follows the appearance of the Tb^{4+} aqueous complex with a potential high enough to oxidize water. Meanwhile, the rate constants in both sections prove to be similar: $k_1^{ch} = (1 \pm 0.3) \times 10^{-1}$ s^{-1}, $k_2^{ch} = (5.0 \pm 0.5) \times 10^{-3}$ s^{-1} (according to chemiluminescence measurements) and $k_1^{sp} = (0.8 \pm 0.3) \times 10^{-1}$ s^{-1}, $k_2^{sp} = (4 \pm 0.4) \times 10^{-3}$ s^{-1} at 298 K (according to spectrophotometry measurements). The two sections are evidently present because of the existence of two isomeric forms of the phosphorotungstate anions [13], which respectively give the two forms of the complexed species dissociating at different rates.

The absorption spectrum of the tetravalent terbium is overlapped by the luminescence spectrum of the $\overset{*}{Tb}{}^{3+}$ ions, hence the desactivation of the latter is quite probable. It turned out that there was not any observable quenching according to the inductive-resonance mechanism, because the $\overset{*}{Tb}{}^{3+}$ desactivation was rather low in the frozen solution (at 77 K) containing $\overset{*}{Tb}{}^{3+}$ and stabilized by the Tb^{4+}–polyphosphorotungstate complex. Therefore, the most probable mechanism of quenching is that due to electron transfer between the Tb^{3+} and Tb^{4+} ions bonded in a complex:

$$\overset{*}{Tb}{}^{3+} + [Tb^{4+} \cdot P_2W_{17}O_{61}{}^{10-}] \xrightarrow{k_q} Tb^{4+} + [Tb^{3+} \cdot P_2W_{17}O_{61}{}^{10-}] \quad (10)$$

Our attempts to obtain the quenching constant were successful with the use of a routine technique of measuring the Tb^{3+} photoluminescence intensities (or τ) at different concentrations of quencher and Tb^{4+}, with the latter being stable, because the $P_2W_{17}O_{61}{}^{10-}$ ion quenches the photoluminescence intensively with concentrations high enough to stabilize Tb^{4+}.

The quenching constant (k_q) may be established in the process of Tb^{4+} ion reduction; *i.e.* under such conditions where the $P_2W_{17}O_{61}{}^{10-}$ concentration is lowered by rapid dilution to give such values at which the Tb^{4+} ions become unstable and, at the same time, at which there exists no complete $\overset{*}{Tb}{}^{3+}$ desactivation by the ligand ions. Therefore, in the course of Tb^{4+} ion reduction it is necessary to observe the kinetics of photoluminescence intensity of the Tb^{3+} ions excited by an external UV radiation source. Here, if an excess amount of the Tb^{3+} ions is introducted into the solution as compared to the Tb^{4+} initial concentration, provided that an increase in the Tb^{3+} concentration due to the Tb^{4+} reduction is neglected, then all the changes in the solution photoluminescence intensity during reaction (3) should be attributed to a decrease in the Tb^{4+} concentration and, at the same time, to the decreasing quenching with that ion.

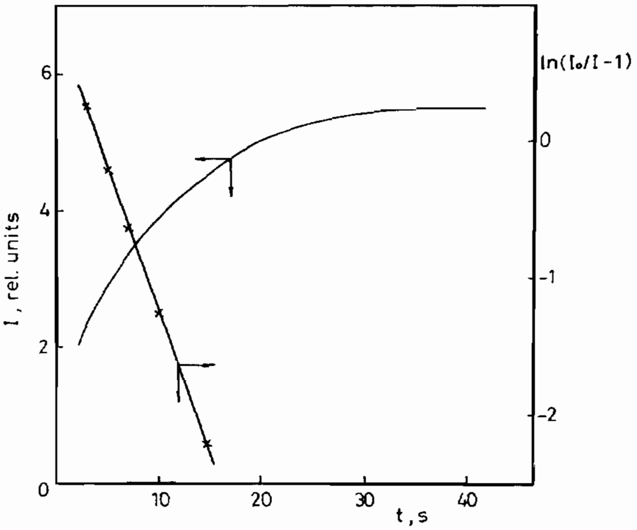

Fig. 3. Changes in the Tb^{3+} photoluminescence intensity with UV excitation (λ = 365 nm) in the reduction of Tb^{4+}. The solution with concentrations of $Tb^{3+} = 4 \times 10^{-3}$ M and $K_{10}P_2W_{17}O_{61} = 4 \times 10^{-3}$ M in 0.1 M H_2SO_4 was instantly diluted ten-fold with the solution of $[Tb^{3+}] = 10^{-3}$ M in 0.1 M H_2SO_4, $T = 298$ K.

This means that the photoluminescence intensity should be minimal at the first moment after dilution of the stable Tb^{4+} solution and the introduction of excess Tb^{3+} ions, and it should increase with the Tb^{4+} ion reduction until the whole amount of the tetravalent terbium is reduced at least to the concentration where its quenching of $\overset{*}{Tb}{}^{3+}$ ions is negligible (Fig. 3). As is obvious, the Tb^{4+} concentration changes exponentially with time:

$$[Tb^{4+}] = [Tb^{4+}]_0(e^{-k_1 t} + e^{-k_2 t}) \quad (11)$$

On investigating the quenching during the reaction, only the registration of the rapid component was successful as the $[Tb^{4+}]$ concentration in the second section, the slower one, of the kinetic curve becomes insufficient to contribute essentially to the quenching process. For that reason, we may take into account the following dependence only:

$$[Tb^{4+}] = [Tb^{4+}]_0 e^{-k_1 t} \quad (12)$$

Substitution of the value from eqn. (12) for $[Tb^{4+}]$ in the Stern–Volmer equation for the quenching of the $\overset{*}{Tb}{}^{3+}$ fluorescence by the tetravalent terbium results in the following expression:

$$I_0/I - 1 = K_s [Tb^{4+}]_0 e^{-k_1 t} \quad (13)$$

where I_0 and I correspond to the photoluminescence intensities (the former corresponds to that following the completion of the reaction, and the latter to a moment t); K_s = quenching constant; k_1 = reaction rate constant. From the linear dependence of $\ln(I_0/I - 1)$ on t (Fig. 3)

$$\ln(I_0/I - 1) = \ln K_s[\mathrm{Tb}^{4+}]_0 - k_1 t \qquad (14)$$

we may obtain both K_s and k_1, the values of which make up $(3 \pm 0.2) \times 10^{-4}$ mol^{-1} s^{-1} and $(2 \pm 0.3) \times 10^{-1}$ s^{-1} respectively at 298 K. The rate constant was found to be higher by the fluorimetry measurements as compared to those from the spectrophotometry and chemiluminescence data, and the difference is explained by the increasing effect of the added Tb^{3+} ions on the rate of the Tb^{4+} complex dissociation with the polyphosphorotungstate ions, because Tb^{3+} itself forms strong complexes with those ions.

The possibility of registring the chemiluminescence despite its low yield ($\eta = 10^{-13}$) may be entirely attributed to a high rate of transformation. The corrections for the $\overset{*}{\mathrm{Tb}}{}^{3+}$ ion desactivation by the polyphosphorotungstate ions and by the Tb^{4+} complexes cannot effectively increase the CL yield, the low value of which evidently takes place due to the quenching of $\overset{*}{\mathrm{Tb}}{}^{3+}$ by the $\mathrm{OH}^{\bullet}$ radicals appearing during the reaction in the immediate proximity of the excited Tb^{3+} ion.

The chemiluminescence brightness may be increased by more than an order if $\mathrm{UO_2}^{2+}$ ions are introduced into the solution, which produce luminescence like the Tb^{3+} ions in the yellow–green region of the spectrum. The kinetics of the luminescence decay remain unchanged. In contrast to the Tb^{3+} ions, the luminescence ability of the uranyl ions in the presence of the polyphosphorotungstate anions reveals no decrease and even shows a tendency to increase. Thus, the photoluminescence intensity of a 10^{-3} M solution of the uranyl ions in 0.1 M of sulfuric acid in the presence of 4×10^{-3} M polyphosphorotungstate anions increases 1.5 times as much as that of Tb^{3+}; the chemiluminescence intensity is reached due to the effective concurrence of the process of energy transfer to the $\mathrm{UO_2}^{2+}$ ions with that of the Tb^{3+} quenching according to the following reaction:

$$\overset{*}{\mathrm{Tb}}{}^{3+} + \mathrm{UO_2}^{2+} \xrightarrow{K} \mathrm{UO_2}^{*2+} + \mathrm{Tb}^{3+} \qquad (15)$$

The rate constant of the energy transfer was calculated with regard to the quenching of the Tb^{3+} ion luminescence by uranyl ions. The dependence of the lifetime of the excited Tb^{3+} ions on the concentration of the uranyl ions is represented as a linear function in the coordinates $\tau_0/\tau - 1 - \mathrm{f}([\mathrm{UO_2}^{2+}])$ (Fig. 4). According to the scheme, the rate constant of the energy transfer from Tb^{3+} to $\mathrm{UO_2}^{2+}$ was calculated as $K_{\mathrm{tr}} = 3.04 \times 10^5$ M^{-1} s^{-1}.

With the reductions of the Tb^{4+} ions, the excited $\overset{*}{\mathrm{Tb}}{}^{3+}$ ions are formed, which can either emit light or be desactivated by the polyphosphorotungstate anions. Addition of the uranyl ions into the solution leads to the third way of desactivating the $\overset{*}{\mathrm{Tb}}{}^{3+}$ ions, *i.e.* transfer of the electron excitation energy to the uranyl ions.

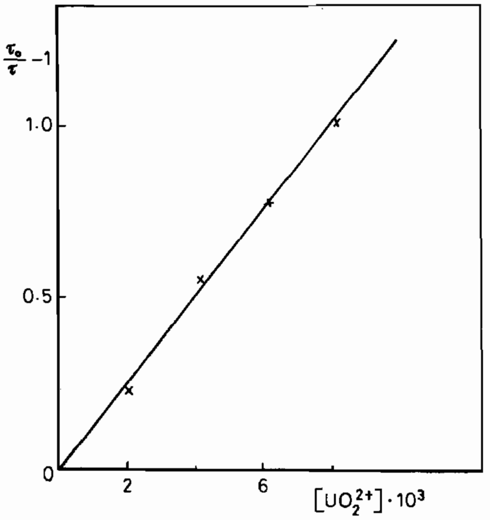

Fig. 4. Dependence of the lifetimes of the excited $\overset{*}{\mathrm{Tb}}{}^{3+}$ ions on the uranyl concentration according to the Stern–Volmer law. $[\mathrm{Tb}^{3+}] = 10^{-2}$ M, $[\mathrm{H_2SO_4}] = 0.2$ M, $T = 298$ K.

The absence of any effect of the uranyl ions on the chemiluminescence kinetics serves as further proof of the excitation of the Tb^{3+} ions in the reduction of the Tb^{4+} aqua-ions only, and that the two sections of the chemiluminescence kinetic curve are not explained by the two-step dissociation of the Tb(IV) phosphorotungstate complexes. Thus, for the first time it has been proved that lanthanide ions can be formed in their excited states not only when they appear in the role of energy acceptors of some chemical reactions [17] in which they do not take any direct part, but also in redox transformations of the ions themselves where electron transfers involving the f-shell occur.

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References

1 N. B. Mikheev, *Radiochimiya, 25*, 642 (1983).
2 P. Gerlikh, Kh. Karras, G. Ketitts and R. Leman, 'Spektroskopitcheskie svoistva aktivirovannykh lazernykh kristallov', Nauka, Moscow, 1966, p. 207.
3 V. A. Arkhangelskaya and P. P. Feofilov, *Zh. Prikl. Spektrosk., 4*, 73 (1966).
4 D. S. McClure and Z. Kiss, *J. Chem. Phys., 39*, 3251 (1963).

5 S. S. Batsanov, V. N. Korobeinikova, V. P. Kazakov and L. I. Kobets, *Opt. Spektrosk.*, *30*, 484 (1971).

6 R. G. Bulgakov, V. P. Kazakov and V. N. Korobeinikova, *Opt. Spektrosk.*, *35*, 856 (1973).

7 V. V. Korolev and N. M. Barhin, *Chem. Phys. Lett.*, *43*, 469 (1976).

8 A. S. Saprykin, V. P. Shilov, V. I. Spitsyin and N. N. Krot, *Dokl. Akad. Nauk SSSR*, *226*, 858 (1976).

9 N. N. Krot, A. S. Saprykin and V. P. Shilov, 'Sposob spektrofotometritcheskogo opredeleniya terbiya', Applied in U.S.S.R. No. 676557, *Bull. Izobretenij*, 28 (1979). International Classification COIF 17/00; GOIN 21/24.

10 B. F. Myasoedov and I. A. Lebedev, *Radiokhimiya*, *19*, 87 (1977).

11 V. P. Kazakov, G. S. Parshin, V. V. Rykova and L. A. Khamidullina, 'O photokhimitcheskom obrazovanii Tb^{4+} i ego reaktsii vosstanovleniya s vozbuzhdenium Tb^{3+}', in 'Tezisy dokladov IV Vsesoyuznogo soveshchaniya po fotokhimii', State Optical Institute, Leningrad, 1976, p. 176.

12 V. P. Kazakov and G. L. Sharipov, 'Radioluminestsentsiya vodnykh rastvorov', Nauka, Moscow, 1986, p. 122.

13 V. I. Spittsyn, M. M. Orlova, N. N. Krot and A. S. Saprykin, *Zh. Neorg. Khim.*, *23*, 1227 (1978).

14 V. P. Gruzdev and V. L. Ermolaev, *Zh. Neorg. Khim.*, *22*, 3022 (1977).

15 S. V. Bel'tyukova, I. S. Poluektov, T. B. Kravtchenko and L. I. Kononenko, *Dokl. Akad. Nauk SSSR*, *242*, 1340 (1978).

16 C. Stein and E. Murzberg, *J. Chem. Phys.*, *62*, 208 (1975).

17 V. A. Belyakov and P. F. Vasil'ev, in 'Molekulyarnaya fotonika', Nauka, Leningrad, 1979, p. 70.