Radiothermoluminescence of tetramethylene sulfoxide

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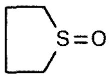
Radiothermoluminescence (RTL) and ESR spectra of tetramethylene sulfoxide (TMSO) irradiated by X-ray and ^{60}Co γ-ray radiation have been studied at 77 K. The temperatures of RTL maxima were correlated with the changes in color of specimens and the shape of the ESR spectral lines. The temperatures at which maxima or inflections are observed (depending on the kind of irradiation, dose, and introduced additives) were determined: 90, 115, 125, 133, 145, and 155 K. A signal of the TMSO radical cation was observed in the ESR spectrum (a singlet with $g = 2.008\pm0.001$ and $\Delta H \approx 12$ Oe); it completely disappeared after the cessation of luminescence at the maximum at 133 K. An analogous result is achieved by illumination of the specimen with maximum effect in the yellow-green region of the spectrum. Activation of RTL by the UO_2^{2+} and Tb^{3+} ions was studied. Their thermal deactivation was correlated with molecular mobility manifested in RTL.

Key words: radiothermoluminescence, radiolysis; sulfoxides, uranium, terbium; thermal deactivation of luminescence.

Sulfoxides are used as efficient extracting agents of ions of transuranium and the other radioactive metals.[1] In this connection it was necessary to study their radiochemical properties. Radiochemical yields of the destruction of sulfoxide groups and formation of sulfides and mercaptans during the irradiation of liquid tetramethylene sulfoxide (TMSO)  have been determined previously.[2] In this work the radiothermoluminescence (RTL) of this compound was studied and compared with temperature changes in the ESR spectra of the paramagnetic particles generated after γ-irradiation at 77 K.

Experimental

TMSO was distilled, stored over a molecular sieve to remove water traces, and distilled again. Before being irradiated, TMSO was placed in a 1 mm layer on the bottom of a platinum dish of 17 mm diameter, kept from atmospheric moisture, and cooled to 77 K. The specimens were irradiated at 77 K either by γ-radiation (^{60}Co) on an "Issledovatel'" installation (dosage rate 10^4 Gy h^{-1}) or by X-ray radiation on an URS-1.0 apparatus (Cu anticathode, $V = 40$ kV, dosage rate $3 \cdot 10^2$ Gy h^{-1}). In the latter case the dish with the specimen was placed before the irradiation flux entering the cryostat through a beryllium window. RTL was recorded on an installation described in Ref. 3 at the heating rate of 5 deg min^{-1}. The specimens were "bleached" after γ-irradiation by illuminating them by a filament lamp (400 W) through a water thermal filter and cut-off light filters (from GOI optical glasses) transmitting the desired part of radiation. The drum of the RTL installation was charged with a set of light filters in the red light. A DRSh-1000 mercury lamp equipped with a LOS-4 illuminant was used for UV-irradiation. Fluorescence spectra were recorded on a Hitachi MPF-4 spectrofluorimeter. ESR spectra and their temperature dependences were recorded on a Radiopan SE/X-2544 spectrometer.

Results and Discussion

TMSO turns violet when γ-irradiated at 77 K (with a maximum of the absorption band at 580 nm). The RTL glow ceases below 200 K and the color disappears simultaneously. The RTL behavior essentially depends on the absorbed dose. The RTL curve after γ-irradiation by doses from 10^3 to 10^4 Gy has its maximum at 433 K and a number of inflections: on the left shoulder at 115 K, and on the right shoulder at 145 and 155 K (Fig. 1). In this case both the shape of the RTL curve and positions of the maxima are well reproducible. RTL is observed in the temperature range from 90 to 180 K after X-ray irradiation, when the absorbed dose is below 10^3 Gy. However, in this case one can obtain a number of curves whose maxima always appear at the same temperatures (90, 115, 133, 145, 155 K), but they change their intensities in each new experiment. The most simple curve of thermoluminescence, with only one maximum at 115 K, is observed after ultraviolet irradiation of TMSO. The shape of the RTL curves is only slightly dependent on the γ-irradiation dose. A large part of the light sum luminesced is accumulated in the dose interval below $5 \cdot 10^3$ Gy (Fig. 2). The RTL brightness has its maximum at a dose of $7 \cdot 10^3$ Gy. The RTL intensity decreases then, which is likely due both

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to the processes of deactivation of the radiation emitter by the primary products of radiolysis and to the effect of the inner filter caused by radiation coloring.

The concentration of paramagnetic particles increases following a more flattened curve (see Fig. 2) as the dose increases. This curve reaches no saturation up to a dose of $4.8 \cdot 10^4$ Gy. No change in the shape and intensity of lines in the ESR spectrum was observed after the specimen was stored for two days after γ-irradiation at 77 K; an intense singlet with $g = 2.008 \pm 0.001$ and $\Delta H \cong 12$ Oe can be picked out from the spectrum (Fig. 3). This component is "bleached" by exposing to visible light of the filament lamp; the procedure had no effect on other parts of the ESR spectrum, *i.e.*, no new paramagnetic particles appear as a result of "bleaching." A band with a maximum at ~600 nm was observed previously in the pulse radiolysis of dimethylsulfoxide, and it was assigned to radical cations.[4] An ESR signal with $g = 2.008$, which appears as a result of the low-temperature radiolysis, was also assigned to radical cations.[5] This allows one to assign the observed singlet and the absorption band with a maximum at 580 nm to the TMSO radical cations. The "bleaching" ESR signal completely disappears when heated to 150 K, *i.e.*, after the cessation of the glow at the maximum at 133 K. The "bleaching" is most efficient in the yellow-green region of visible spectrum. The violet color, acquired by TMSO

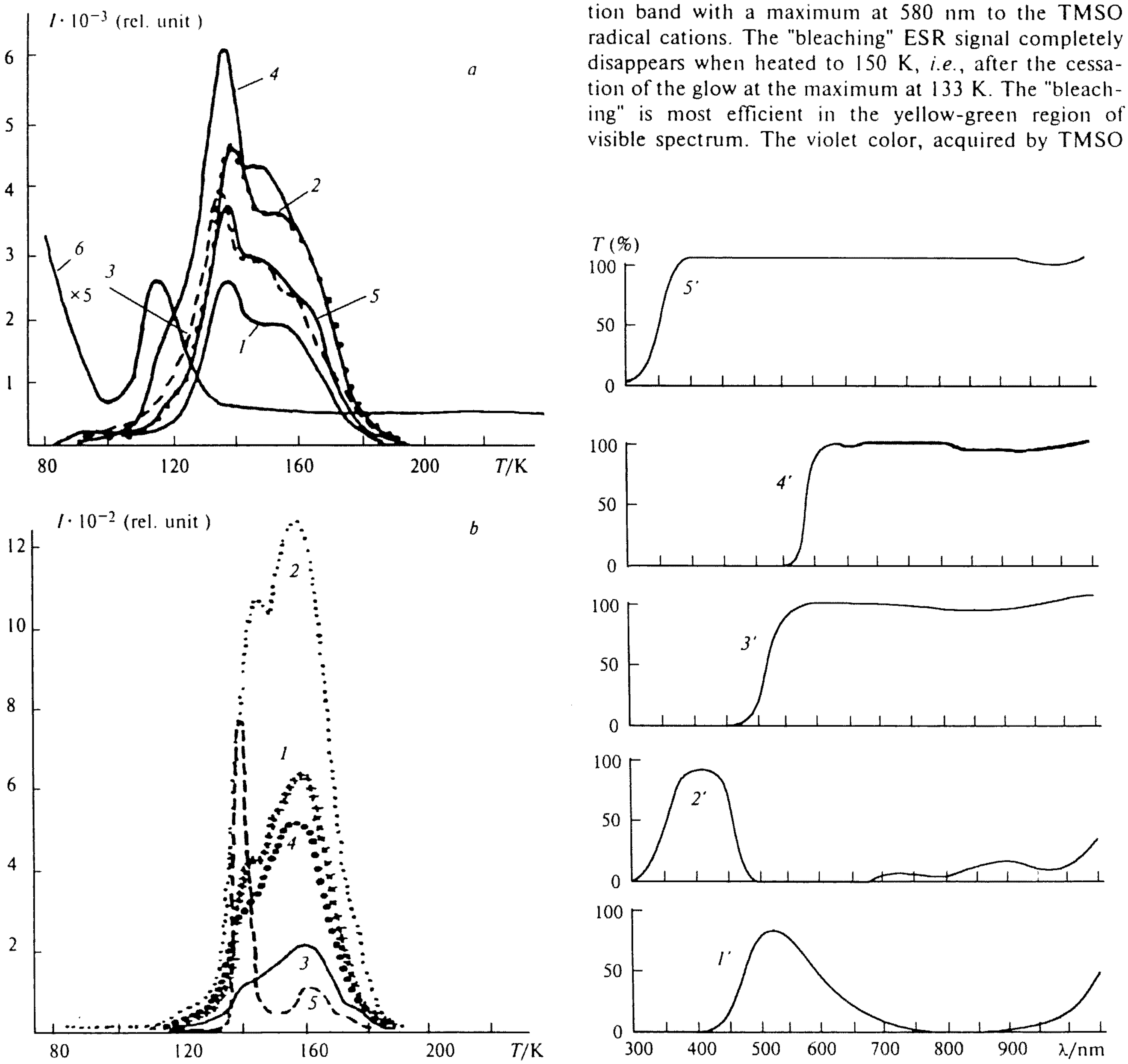


Fig. 1. RTL curves of TMSO: *a*, ^{60}Co γ-irradiated at 77 K; absorbed dose $D \cdot 10^{-3}$ Gy: 2.5 (*1*); 5 (*2*); 7.5 (*3*); 10 (*4*); 30 (*5*); *6*, the RTL curve of TMSO after ultraviolet irradiation; *b*, after "bleaching" during 15 min by a part of the spectrum (curves *1*—*5*) cut from the filament lamp light by the light filters with known transmission spectrum (curves *1′*—*5′*); the absorbed dose of γ-irradiation is 10^4 Gy.

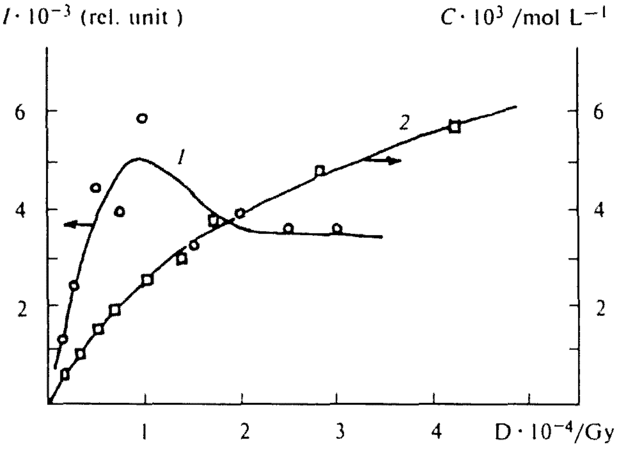


Fig. 2. Dependence on the absorbed dose (D) of γ-irradiation: *1*, intensity of the TMSO radiothermoluminescence; *2*, concentration of paramagnetic particles (*C*).

upon γ-irradiation, disappears if the specimen is "bleached" and annealed to 150 K. The color turns brown, but it only exists in the narrow temperature interval from 150 to 180 K and disappears simultaneously with the cessation of the RTL glow. It is likely that the same particles are responsible for the ESR singlet, the violet color, and the RTL maximum at 133 K. These particles might be TMSO radical cations, captured electrons, and/or radical anions as counterions.

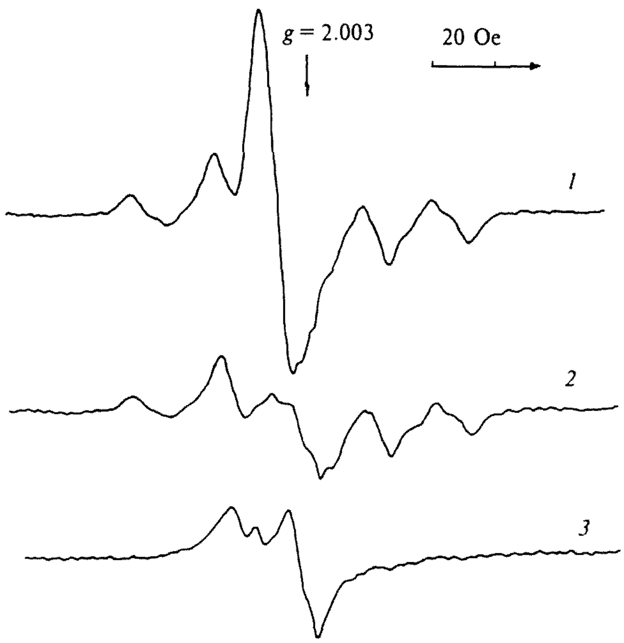


Fig. 3. ESR spectra of TMSO, X-ray irradiated at 77 K (dose of $6 \cdot 10^{-2}$ Gy); *1*, immediately after irradiation; *2*, "bleached" by the filament lamp light during 10 min; *3*, heated for 3 min at 187 K after X-ray irradiation. The spectra were recorded at 77 K.

A multiplet ESR signal, which is characterized by $g \cong 2.003$, a splitting of ≈25 Oe, and a total extent of ≈130 Oe, remains after temperature annealing to 150 K or "bleaching" by visible light. Four extreme (symmetric with respect to each other) components of this signal are clearly seen in the initial spectrum of γ-irradiated TMSO, whereas all five components are seen in the specimen "bleached" by visible light (see Fig. 2). The quintet was tentatively assigned to a radical formed as a result of abstraction of the hydrogen atom from the TMSO molecule. In this case the observed multiplet can be due to the interaction of the unpaired electron with one α-proton and two β-protons ($A_\alpha = A_\beta^{(1)} = 1/2A_\beta^{(2)} \cong 25$ Oe). The abstraction of the hydrogen atom in the α-position is common to the radiolysis of heterocyclic compounds.[6] Further changes occur in the ESR spectrum of TMSO γ-irradiated at 77 K (including that "bleached" by visible light) in the process of thermal annealing; they are completed at 183 K with the appearance of an anisotropic signal with $g_1 = 2.020$, $g_2 = 2.010$, and $g_3 = 2.003$ (see Fig. 2). This signal exists up to 206 K. The general view of the spectrum, values of *g*-factor, and high thermostability of the particles responsible for this spectrum allows one to assign it to the sulfinyl radical of the RSO• type; the latter were previ-

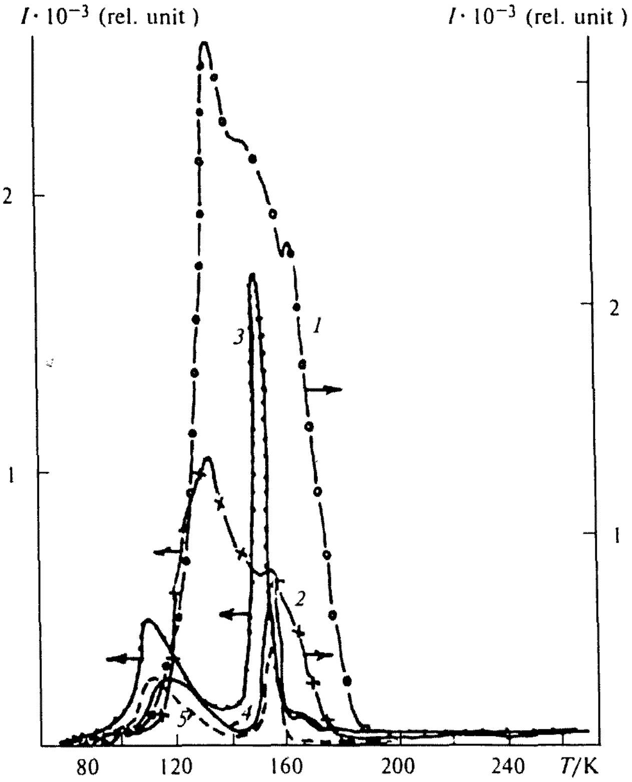


Fig. 4. The effect of water additives on the TMSO radiothermoluminescence. The RTL curves after γ-irradiation (10^4 Gy) with the following water content in TMSO (%): 0.1(*1*); 0.5 (*2*); 2.5 (*3*); 5 (*4*); 10 (*5*).

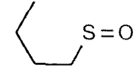
ously generated chemically[7] in the liquid phase for a number of sulfoxides and were observed after γ-irradiation of dimethylsulfoxide.[8] This signal, as well as the brown color, completely disappears when heated to 206 K, which might be due to the RTL glow at the second, poorly resolved maximum.

The RTL maxima are likely to be associated with a release of the molecular mobility, as it was demonstrated in one of the first works on polymers[9] and confirmed for many other systems[10] including those with participation of dimethylsulfoxide.[11] Relaxation and phase transitions are not always clearly recorded if diffraction or differential-thermal methods are used. Thus, only one of these transitions for TMSO was recorded at 223.9 K.[12] In the same work, the TMSO melting point is given (231.8 K). At the same time, TMSO, like some other sulfoxides, is prone to overcooling, and the temperatures of their solidification (as well as those of melting) are acutely sensitive to impurities. The value of temperature we obtained (281 K) differs from those reported in the literature. The melting points for other sulfoxides, including those containing the dimethyl radicals, lie also above 0° C. These discrepancies must be addressed.

It should be noted that radiothermoluminescence of TMSO is highly sensitive to water admixtures (Fig. 4). Deformation of the radiothermoluminescence curve of TMSO is pronounced if only 0.1% of water is added. An increase in the water content to 1—2% results in a drastic change of the shape of the curve. Higher concentrations of water have little effect on the shape of the RTL curve and only decrease the brightness of radiothermoluminescence of the solution. A narrow peak with a maximum at 153 K (characteristic of pure water) is clearly seen on the RTL curve of the water-containing sulfoxide.[13]

The radiothermoluminescence of TMSO is equally sensitive to the radiolysis products accumulated in the course of irradiation process, which is particularly pronounced at doses of tens of Mrad (see Fig. 1). The irradiation increases the viscosity of the liquid sulfoxide due to the formation of dimers,[2] which results in a change in relaxation properties of the solution.

The shape of the RTL curve is also changed upon introduction of uranyl acetate in TMSO. In this case the brightness of the main maximum increases, but it begins decreasing drastically when the concentration of the UO_2^{2+} ions exceeds 10^{-2} mol L^{-1}. The shape of the radiothermoluminescence curve begins changing somewhat earlier, even at the uranyl content $>10^{-3}$ mol L^{-1}. The dissolved UO_2^{2+} ion decreases the brightness of the high-temperature shoulder of the RTL curve (Fig. 5) to a greater degree. Another consequence of the uranyl introduction is the change in the radiation emitter.

The RTL emitter in pure sulfoxides has not been identified as yet. One fails in detecting their photoluminescence both at room temperature and at 77 K. The color of alkylsulfoxides after γ-irradiation depends on the length of the hydrocarbon radical. The spectral regions of RTL of alkylsulfoxides also differ. Thus, the RTL of diethylsulfoxide lies in the range from 500 to 700 nm, whereas a weakening of luminescence by cut-off light filters (most pronounced in the blue-green region) is observed for γ-irradiated TMSO (Fig. 6). The spectral composition depends on the temperature at which the recombination processes proceed. Thus, the green component of the TMSO radiothermoluminescence is represented on the initial rising part of the curve in a lesser degree than on the succeeding parts. If one assumes that the recombination processes in sulfoxides are similar, then, referring to previously published works,[13,14] one might accept the excited  radical anion as the emitter of RTL. Identification of the RTL emitter of the UO_2^{2+} solutions in TMSO is more reliable: it is the excited uranyl ion which is the energy acceptor of the recombination processes. The weakening of the RTL intensity at all temperatures lies just in the region of fluorescence of this ion (from 480 to 560 nm, see Fig. 6). It is likely that this ion or the products of its

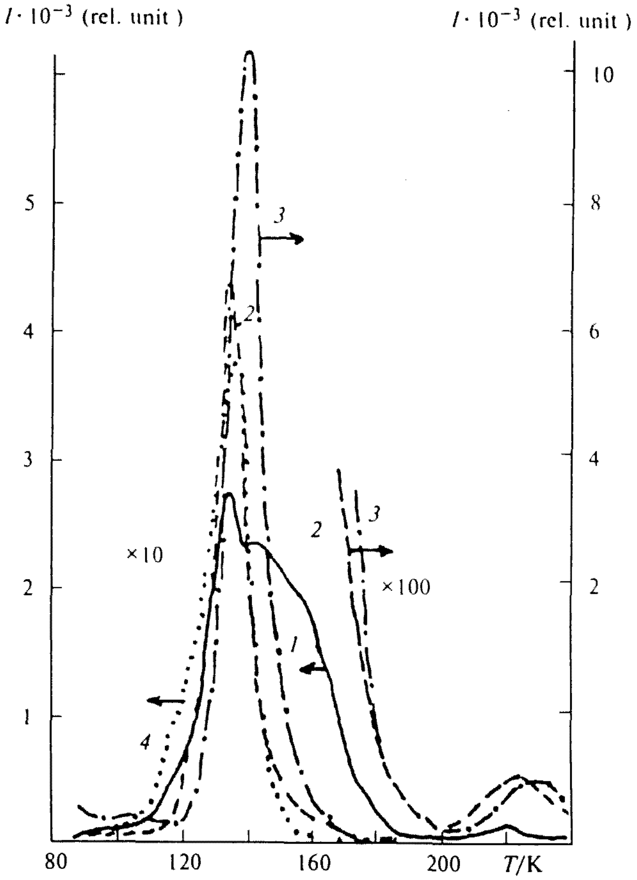


Fig. 5. RTL of the uranyl acetate solutions in TMSO after γ-irradiation (dose of 10^4 Gy) at the following UO_2^{2+} concentrations (mol L^{-1}): 10^{-3} (*1*); $4 \cdot 10^{-3}$ (*2*); 10^{-2} (*3*); 10^{-1} (*4*).

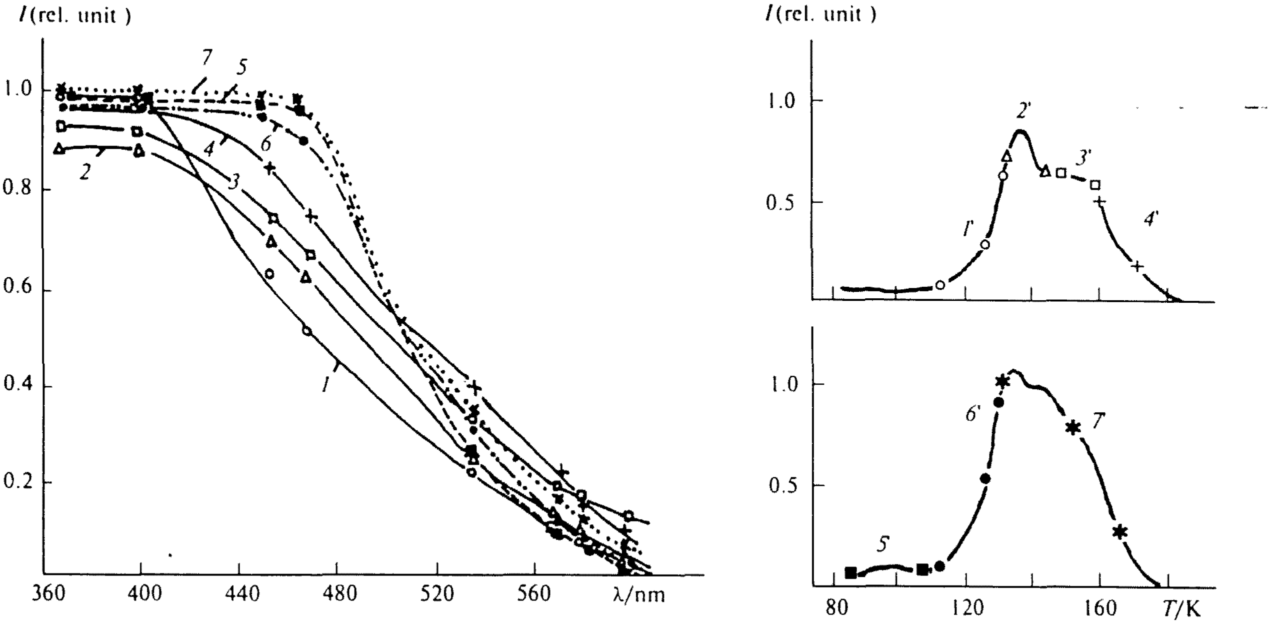


Fig. 6. Spectral region of the RTL glow of TMSO (curves *1—4*) and of the UO_2^{2+} solutions in TMSO (curves *5—7*) on different parts of the RTL curves denoted by figures *1'—4'* and *5'—7'*.

low-temperature radiolysis (for instance, the UO_2^+ ion) participate in low-temperature chemiluminescent reactions, which is in agreement with the change in the shape of the RTL curve. At the same time, the luminescence is detected at higher temperatures when the solution is already a melt. It is, of course, the chemiluminescence of the products of radiolysis,[15] since its brightness increases as the uranyl concentration increases (Fig. 7). At the same time, the RTL brightness is sharply weakened if the concentration of UO_2^{2+} ions exceeds 10^{-2} mol L^{-1}. The uranyl ion plays a dual role: on the one hand, it is the energy acceptor and therefore the RTL brightness increases to a certain value with increase in its content in the solution; on the other hand, it is the electron acceptor, which is why the RTL brightness decreases when the efficiency of the electron capture in the course of radiolysis begins dominating over activation. Indirect confirmation of such behavior are data on activation of the TMSO radiothermoluminescence by Tb^{3+} ions. This ion has equally bright photoluminescence in the visible region as UO_2^{2+}; however, it is not so efficient in capturing the electrons and can only play the role of the energy acceptor of recombination processes. Therefore, a smooth increase in the RTL brightness is observed with increase in its concentration; the RTL brighness is rapidly saturated already at a content of Tb^{3+} ions $>2 \cdot 10^{-3}$ mol L^{-1}, as it should be for activated RTL (see Fig. 7).

Introduction of terbium ions into a solution results in lesser deformations of the RTL curves as compared to those in UO_2^{2+} solutions. A number of inflections on the low-temperature shoulder is more distinctly located (103, 115, and 125 K), the same is true for case the maximum at 220 K; the whole RTL curve is more similar to that for inactivated TMSO and differs only in its higher intensity (Fig. 8).

Phase and relaxation transitions in TMSO in the low-temperature range, where RTL is observed, have not been studied up to the present. However, they reveal themselves not only in RTL but also in the temperature

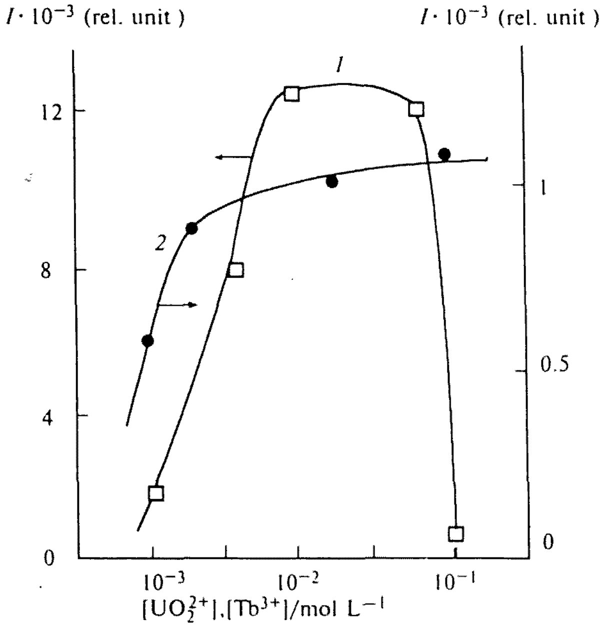


Fig. 7. Dependence of the RTL brightness of the TMSO solutions on the UO_2^{2+} (curve *1*) and Tb^{3+} (curve *2*) concentrations.

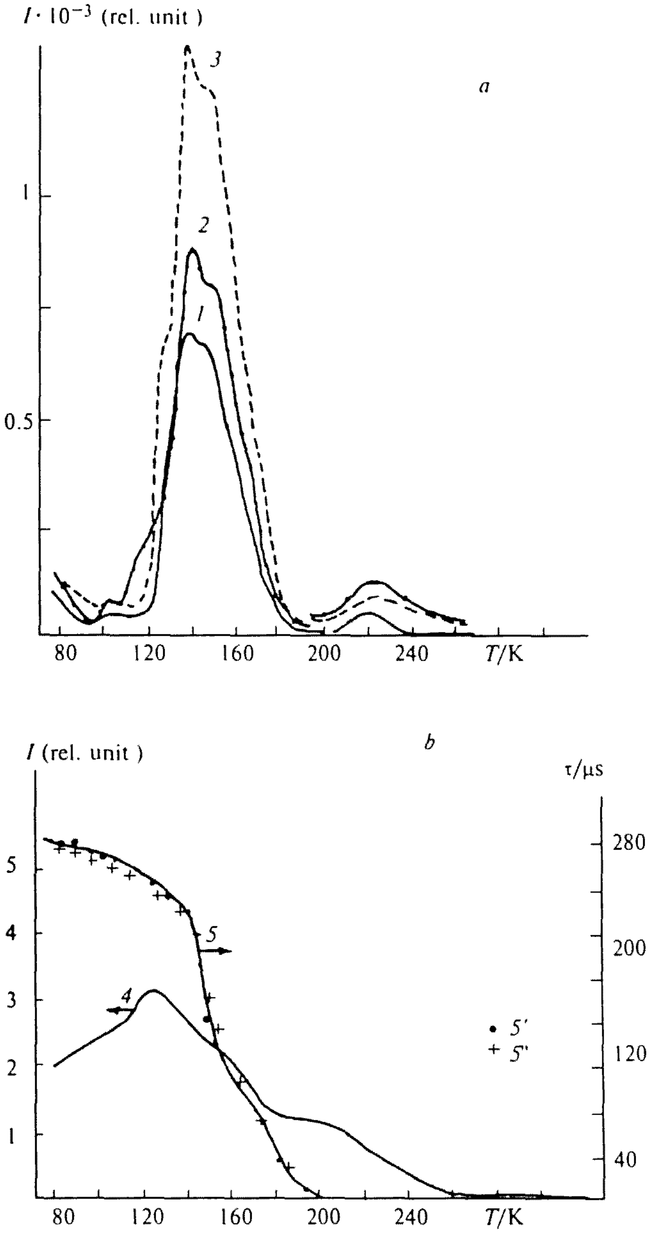


Fig. 8. *a* — Radiothermoluminescence of the TMSO solutions at the following concentrations of Tb^{3+} ions (mol L^{-1}): 10^{-3} (*1*), $2 \cdot 10^{-3}$ (*2*), $2 \cdot 10^{-2}$ (*3*); *b* — temperature dependences of the photoluminescence intensity of Tb^{3+} ions in the TMSO solutions (*4*) and lifetime (*5*) in the excited state of the UO_2^{2+} ions in the nonirradiated solution in TMSO (*5*) and those in the X-ray irradiated solution (*5'*) (dose of $3 \cdot 10^2$ Gy).

dependence of the intensity of photoluminescence of Tb^{3+} and UO_2^{2+} ions (see Fig. 8). Thus, photoluminescence of Tb^{3+} ions begins increasing with increasing temperature from 77 K contrary to the expected decrease due to the temperature quenching. This behavior of lanthanide and uranyl ions is explained by phase transitions in the matrix of frozen solution.[15] The monotonous rise becomes steeper when the temperature approaches 115 K (the temperature of one of the inflections on the RTL curve). The intensity maximum of fluorescence of terbium ions falls on the temperature of the next inflection of the RTL curve of TMSO. This is in agreement with the assumption that it is the phase transitions and recombination processes stimulated by them that are the main reason for the formation of the RTL maxima. It is difficult to state whether it can be an exhaustive explanation of all the peculiarities of RTL. For example, if one introduces a correction for the thermal deactivation of uranyl and terbium ions, the shape of the RTL curve will change somewhat, since the yield of the photon luminescence in the temperature range of the dip of the RTL main maximum is much lower than that at its left shoulder. This is of particular importance for solutions of uranyl ions whose lifetime in the excited state changes slightly with increasing temperature in the interval from 77 to 145 K (see Fig. 8) and sharply decreases after reaching the temperature of one of the poorly resolved RTL maxima.

No differences in the temperature changes of the lifetimes of the excited UO_2^{2+} ions for irradiated and nonirradiated solutions were observed. The experimental points of both dependences lie on the same curve (see Fig. 8) and, hence, no deactivation of the excited uranyl ions by the radiolysis products occurs.

References

1. Yu. I. Murinov, V. N. Maistrenko, and N. G. Afzaletdinova, *Ekstraktsiya metallov S,N-organicheskimi soedineniyami* [*Extraction of Metals with S,N-Organic Compounds*], Nauka, Moscow, 1993, 192 pp. (in Russian).
2. V. N. Korobeinikova, G. G. Bikbaeva, Yu. I. Murinov, Yu. E. Nikitin, and V. P. Kazakov, *Radiokhimiya* 1983, 281 [*Sov. Radiochem.*, 1983 (Engl. Transl.)].
3. V. N. Korobeinikova, Yu. N. Chuvilin, K. S. Minsker, I. G. Kovel'zon and V. P. Kazakov, in *Khimiya i fiziko-khimiya vysokomolekulyarnykh soedinenii* [*Chemistry and Physico-Chemistry of High-Molecular Compounds*], BF AN SSSR, Ufa, 1975, 148 (in Russian).
4. A. K. Pikaev, *Sovremennaya radiatsionnaya khimiya. Radioliz gazov i zhidkostei* [*Modern Radiochemisry. Radiolysis of Gases and Liquids*], Nauka, Moscow, 1986, 440 pp. (in Russian).
5. M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1976, 908.
6. S. Ya. Pshezhetskii, A. G. Kotov, V. K. Milinchuk, V. A. Roginskii, and V. I. Tupikov, *EPR svobodnykh radikalov v radiatsionnoi khimii* [*ESR of Free Radicals in Radiochemistry*], Khimiya, Moscow, 1972, 480 pp. (in Russian).
7. B. C. Gilbert, C. M. Kirk, R. O. C, Norman, and M. A. N. Lame, *J. Chem. Soc., Perkin Trans. 2*, 1977, 497.
8. J. C. Machado, R. Debuyst, F. Dejehet, and D. Apers, *Radiochem. Radioanal. Lett.*, 1972, **9**, 353.
9. V. G. Nikol'skii and N. Ya. Buben, *Dokl. Akad. Nauk SSSR*, 1960, **134**, 134 [*Dokl. Chem.*, 1960, **134** (Engl. Transl.)].
10. V. G. Nikol'skii, *Khim. Vys. Energ.*, 1968, **2**, 271 [*High Energy Chem.*, 1968, **2** (Engl. Transl.)].

11. V. P. Kazakov, V. N. Korobeinikova, D. D. Afonichev, Yu. E. Nikitin, and V. I. Ionov, *Zh. Prikl. Spektr.* [*J. Appl. Spectrosc.*], 1978, **29**, 633 (in Russian).
12. J. D. Haines, and F. R. Gilson, *J. Chem. Soc. Faraday Trans.*, 1990, **86** (14), 2617.
13. N. M. Shishlov, V. N. Korobeinikova, V. A. Mazunov, A. A. Panasenko and R. A. Sadykov, *Khim. Vys. Energ.*, 1983, **17**, 179 [*High Energy Chem.*, 1983, **17** (Engl. Transl.)].
14. V. N. Korobeinikova, N. M. Shishlov, R. A. Sadykov, V. P. Kazakov, and A. A. Panasenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1914 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31**, No.8 (Engl. Transl.)].
15. V. P. Kazakov, *Khemilyuminestsentsiya uranila, lantanoidov i d-elementov* [*Chemiluminescence of Uranyl, Lanthanides, and d-Elements*], Nauka, Moscow, 1980, 178 pp. (in Russian).

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