# EFFECT OF COMPLEX FORMATION IN THE DIOXYETHANE—Eu(fod)$_3$—KETONE SYSTEM ON EUROPIUM(III) DEACTIVATION PROCESSES

**S. S. Ostakhov,**
**G. L. Sharipov, V. P. Kazakov,**
**and G. A. Tolstikov**

UDC 541.49:547.718+546.21+547.518:546.661:541.141.7:535.379

*It was established that the quenching of Eu(fod)$_3$* luminescence by dioxyethanes is chemical in character and caused by formation of [dioxyethane...Eu(III)] complexes. A τ-metric method was proposed for testing the possibility of catalysis of thermal decomposition of dioxyethanes by lanthanide ions and for monitoring dynamics of complex formation in the dioxyethane—lanthanide—ketone chemiluminescent system.*

Compounds of Eu(III) have characteristic emission spectra with a high luminescence yield and are frequently used as activators of luminescence. Chemical excitation of Eu(III) has been observed in the oxidation of hydrocarbons by oxygen [1], during interaction of peroxides with aromatic amines [2], and during thermal decomposition of dioxyethanes [3]. In all these reactions the Eu(III) ions are not directly involved, being excited only as a consequence of radiationless transfer of energy from products of the chemical conversions. However, a number of lanthanide chelates may not only sensitize chemiluminescence of dioxyethanes but also effectively catalyze their decomposition [4, 5]. The catalytic decomposition is also accompanied by excitation of the lanthanide ions. The mechanism of energy transfer from the potential source of excited states, a dioxyethane molecule, to a lanthanide ion in the conditions of the catalytic process, which is based on complex formation, is not clear in many respects.

Methods have been developed [6, 7] to study complex formation of lanthanide ions with various ligands based on analysis of the luminescence yield and attenuation time of these ions. These methods were used in this work to study processes of radiationless energy transfer in the system dioxyethane—Eu(III)—ketone in complex-forming conditions.

## EXPERIMENTAL

Adamantylideneadamantane-1,2-dioxyethane(I) and tetramethyl-1,2-dioxyethane(II) were synthesized as described previously [8, 9]. Adamantanone(III) was purified by sublimation; especially pure grade acetone(IV) and scintillation grade xylene were used without further purification. Solutions of tris(1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate)europium (Eu(fod)$_3$) were prepared by dissolving a weighted portion of the substance in xylene. All operations were carried out in an argon atmosphere. The lifetime of Eu(fod)$_3$* in the excited state (τ) was determined from analysis of attenuation curves of the luminescence intensity produced by irradiation of the specimen with an LGI-21 pulse nitrogen laser ($T$ = 20 nsec, $\lambda_e$ = 337 nm). The FEU-79 signal was recorded on the screen of an S1-70 oscillograph. Solutions were cooled down to the experimental temperature with liquid-nitrogen vapor. Intensity measurements and recordings of chemiluminescence (CL) spectra were made using the apparatus described previously [10]. Photoluminescence (PL) spectra were obtained in a Hitachi MPF-4 spectrometer.

---

Institute of Chemistry, Bashkir Science Center, Urals Branch of the Academy of Sciences of the USSR, Ufa.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1745-1750, August, 1990. Original article submitted July 7, 1989.

0568-5230/90/3908-1581$12.50

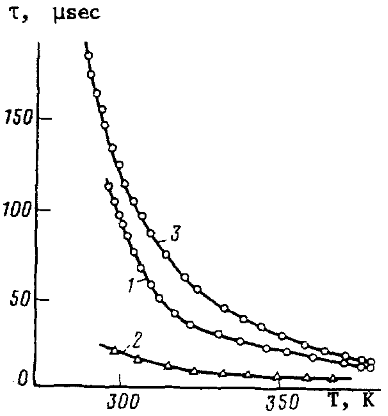


Fig. 1

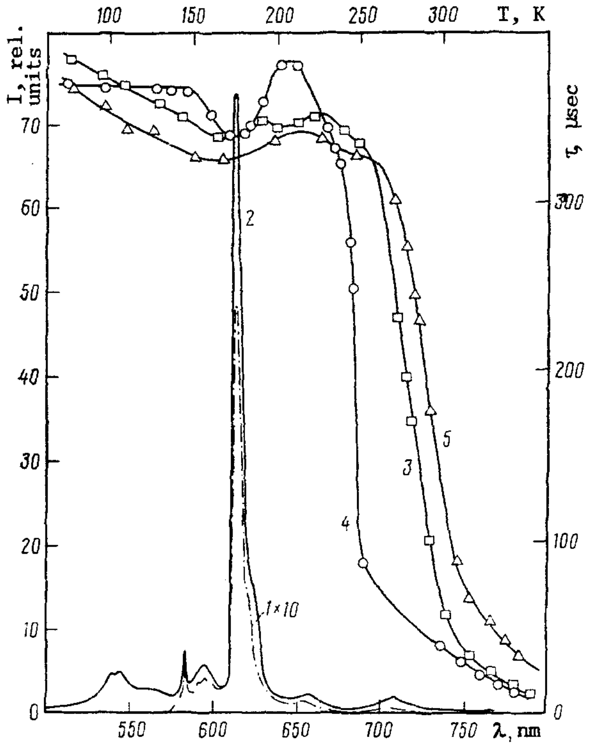


Fig. 2

Fig. 1. Temperature dependence of τ for Eu(III)* ($10^{-2}$ M) in xylene: (1) no additives; (2) $4 \cdot 10^{-2}$ M (I); (3) $5 \cdot 10^{-3}$ M (III).

Fig. 2. Photoluminescence spectra of Eu(III)* ($5 \cdot 10^{-2}$ M): (1) no additives; (2) 0.1 M (I). Temperature dependence of τ for Eu(III)* ($10^{-2}$ M): (3) no additives; (4) $5 \cdot 10^{-3}$ M (III).

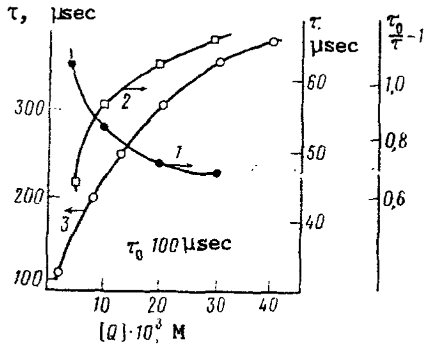


Fig. 3. Dependence of τ for Eu(fod)$_3$* ($10^{-2}$ M) on concentration of adamantanone (3) and of dioxyethane (I) (1) in xylene, and the same in Stern–Volmer coordinates (2).

## RESULTS AND DISCUSSION

A study was carried out on the dependence of the lifetime of Eu(fod)$_3$* in xylene on the presence of (I) and (II) and their thermolysis products (III) and (IV). It was found that addition of (I) to a Eu(fod)$_3$ solution in xylene (298 K) leads to quenching of the luminescence of the Eu(III)* ion (Fig. 1). There is a decrease in both luminescence yield and in $\tau$ for Eu(III)* (from 100 to 15 $\mu$sec). The absorption spectra of (I) and (II) do not overlap with the Eu(III)* PL spectrum, i.e., radiationless energy transfer is not very likely, and quenching is due to chemical processes. The chemical character of the interaction of dioxyethane with the Eu(fod)$_3$ complex is corroborated by a change in the Eu(III)* PL spectra (a new band at 535 nm (Fig. 2)). Attenuation of the luminescence in the presence of (I) is nonexponential and the quenching kinetics do not obey the Stern—Volmer law (Fig. 3). The absence of such a relationship implies an association between an excited donor and a nonexcited acceptor [7].

The results obtained make it possible to explain quenching of Eu(III)* luminescence by formation of a [Eu(III)...(I)] complex

$$\mathrm{Eu(III)} + h\nu_0 \longrightarrow \mathrm{Eu(III)}^* \tag{1}$$

$$\mathrm{Eu(III)} + \mathrm{(I)} \rightleftharpoons [\mathrm{Eu(III)}\cdots\mathrm{(I)}] \tag{2}$$

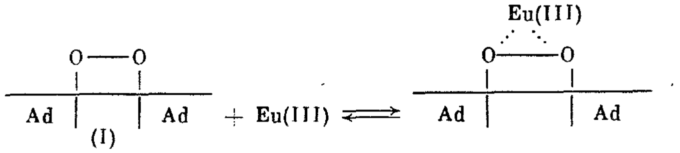
$$[\mathrm{Eu(III)}\cdots\mathrm{(I)}] + h\nu_0 \longrightarrow [\mathrm{Eu(III)}\cdots\mathrm{(I)}]^* \tag{3}$$

$$\mathrm{Eu(III)}^* + \mathrm{(I)} \rightleftharpoons [\mathrm{Eu(III)}\cdots\mathrm{(I)}]^* \tag{4}$$

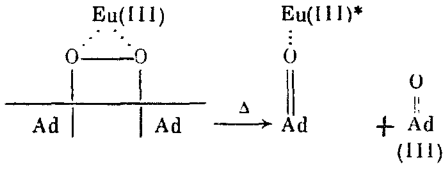
$$\mathrm{Eu(III)}^* \longrightarrow \mathrm{Eu(III)} + h\nu_1 \tag{5}$$

$$[\mathrm{Eu(III)}\cdots\mathrm{(I)}]^* \begin{cases} \longrightarrow [\mathrm{Eu(III)}\cdots\mathrm{(I)}] + h\nu_2 & \text{(6a)} \\ \longrightarrow \mathrm{P}^* \longrightarrow \mathrm{P} + h\nu_3 & \text{(6b)} \end{cases}$$

Deactivation of the excited complex may occur not only by way of physical emission (reaction 6a), but also as a consequence of chemical restructuring (decomposition of the dioxyethane ligand). Deactivation in reaction (6b) is more complex, the dioxyethane decomposing to form a new excited product (P). Dioxyethanes may coordinate with Eu(fod)$_3$ via oxygen atoms (reaction (7)). Formation of a complex, in its turn, causes a redistribution of electron density in the dioxyethane molecule which facilitates rupture of the strained O—O bond (reaction (8)), thereby catalyzing thermal decomposition of the dioxyethanes (Table 1) [4, 5]



(7)



(8)

where Ad represents adamantane.

We suggest that during excitation of the [Eu(III)...(I)] complex the catalytic process of decomposition of (I) within the complex rapidly accelerates. Evidence in support of this is provided by data on the decomposition of dioxyethanes under the influence of different types of energy [11]. Anti-Stokes sensitization of dioxyethane decomposition is a well-known example [12].

Thus, complex formation leads to substitution of solvent molecules in the immediate environment of the Eu(III)* ion by dioxyethane molecules and a change in the probability of radiationless transitions and, therefore, also in $\tau$ for Eu(fod)$_3$*. It should be noted that the absence of Eu(III)* quenching by the dioxyethane in frozen solid solutions of xylene (Fig. 2) can be explained by a displacement of equilibrium (2) towards lower concentrations of the [Eu(III)...(I)] complex as the temperature is lowered.

TABLE 1. Activation Parameters for Thermal Decomposition of Dioxyethanes in Xylene

| $[Eu(fod)_3]\cdot 10^3$, M | T, K | $k\cdot 10^5$, $sec^{-1}$ | $E$, kJ/mole | $\Delta S^{\neq}$, eu |
|---|---|---|---|---|
| | | Adamantylideneadamantane-1,2-dioxyethane | | |
| 0 | 325–359† | – | 145±2,5 | – |
| 5 | 366 | 5,95±0,5 | 125±8,4 | 2,6±0,8 |
| | 377 | 22,9±0,8 | | |
| | 389 | 68,9±1,7 | | |
| | | Tetramethyl-1,2-dioxyethane | | |
| 0 | 326 | 3,9±0,2 | 115±12,5 | 2,2±0,8 |
| | 337 | 13,2±0,3 | | |
| | 348 | 38,1±0,3 | | |
| | 357 | 153,0±0,8 | | |
| 10 | 316 | 98,0±0,2 | 83±10,9 | −11,8±2,6 |
| | 319 | 125,4±3,3 | | |
| | 328 | 400.5±3,6 | | |
| | 336 | 581,5±20,4 | | |

---

†In this temperature range the rate of decomposition of (I) is low and entropy and $k$ values were not determined; $E$ was found from the temperature dependence.

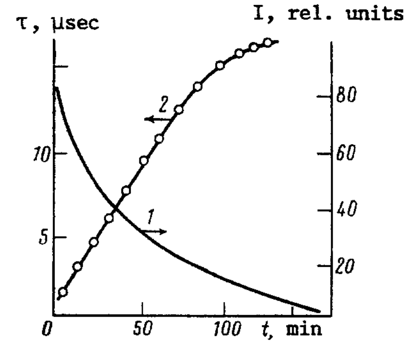


Fig. 4

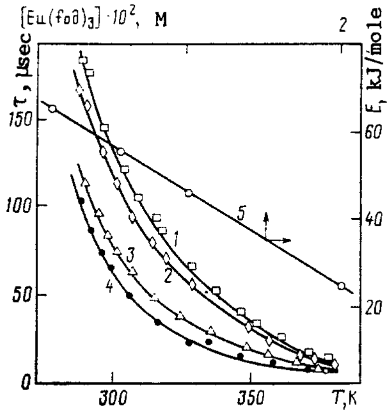


Fig. 5

Fig. 4. Kinetic relationships of CL decomposition of (I) ($4\cdot 10^{-2}$ M) at 353 K in the presence of $Eu(fod)_3$ (1) and the PL $\tau$ for $Eu(fod)_3^*$ (2).

Fig. 5. Temperature dependences of $\tau$ for Eu(III) ($[Eu(fod)_3]\cdot 10^3$ M): (1) 1; (2) 2; (3) 10; (4) 20; also activation energy of $\tau$ for Eu(III)* quenching as a function of $[Eu(fod)_3]$.

Accordingly, from the change in lifetime in the excited state of the lanthanide ion, being a sensitizer of CL dioxyethane decomposition, it may be established whether it will affect the stability of the latter. Thus, the presence of (II) causes a significant decrease in $\tau$ for the $Eu(fod)_3^*$ complex in xylene and catalysis occurs during sensitization of CL decomposition of (II) (Table 1). On the other hand, addition of (II) to a solution of $Eu(NO_3)_3\cdot 6H_2O$ in xylene and (I) to a solution of $Tb(NO_3)_3\cdot 5H_2O$ in acetonitrile does not cause changes in $\tau$ and they should not affect the thermal stability of dioxyethanes. In fact, as has been shown previously [10], terbium nitrate does not affect the activation parameters during activation of CL decomposition of (I). The activation energy for decomposition of (II) in the presence of europium nitrate was 115 kJ/mole ($\Delta S^{\neq}$ = 2.53 eu), i.e., the same as that with no additives [9], and the role of $Eu(NO_3)_3\cdot 6H_2O$ therefore comes down to sensitization of acetone PL. The absence of catalysis of the thermal decomposition of (I) and (II) by $Tb(NO_3)_3\cdot 5H_2O$ and $Eu(NO_3)_3\cdot 6H_2O$ then may be due to the presence of $H_2O$

molecules in the coordination sphere of the lanthanide ions preventing complex formation with the dioxyethanes. In fact, addition of water to the dried solutions leads to a decrease in the $\tau$-reduction effect for Eu(fod)$_3$* in the presence of (I) (Figs. 1 and 2).

The products of decomposition of (I) and (II), the ketones (III) and (IV), effectively sensitive PL of Eu(fod)$_3$*. The lifetime of Eu(fod)$_3$* in xylene (298 K) increases in the presence of (III) to 135 $\mu$sec (Fig. 1). There is a similar character to the change in $\tau$ on when acetone ($1.5 \cdot 10^{-2}$ M) is added to a Eu(fod)$_3$ solution ($10^{-2}$ M) in xylene (298 K): the lifetime of Eu(III)* increases to 230 $\mu$sec. The linear dependence of $\tau$ on the concentration of (III) in the $10^{-3}$-$10^{-2}$ M range (Fig. 3) indicates that Eu(fod)$_3$ apparently forms an adamantanone complex of 1:1 stoichiometric composition. This is in agreement with NMR data regarding the formation of a complex in the ground state [13].

The dynamics of the effect of complex formation on $\tau$ for Eu(fod)$_3$* may be followed in the course of thermolysis of (I) (Fig. 4). This figure shows the kinetics of decomposition of (I), which is catalyzed by the europium(III) complex, measured with respect to CL intensity (curve 1) and for Eu(fod)$_3$* (curve 2). The increase in $\tau$ for Eu(fod)$_3$* in thermolysis of (I) is due to two factors: first, thermal decomposition of the quenching agent, (I); second, formation of an adamantanone which increases $\tau$ for Eu(III)*. Attainment of saturation on curve (2) corresponds to complete decomposition of the dioxyethane. Thus, observation of the variation in $\tau$ for Eu(III)* in the course of thermolysis of a dioxyethane serves as a method for monitoring the progress of the reaction and the dynamics of complex formation in the system under investigation.

In investigations of complex formation between Eu(fod)$_3$* and dioxyethanes and ketones it is necessary to take into account quenching of Eu(fod)$_3$* PL when its concentration is increased. At present the main theories explaining the nature of concentration quenching are a molecular association theory and inductive-resonance migration of excitation energy [14]. These two viewpoints are not mutually exclusive, however, but supplement each other.

We carried out an investigation of concentration quenching of Eu(fod)$_3$* in xylene in parallel with the study of quenching during temperature increase. Figure 5 shows the relationships of temperature quenching of $\tau$ for Eu(fod)$_3$* at different Eu(fod)$_3$ concentrations. If concentration quenching is displayed to a significant extent at room temperature, then temperature quenching takes on a dominant role on raising the temperature. At 388 K concentration quenching is not observed against a background of temperature quenching. On the other hand, there is a decrease in the activation energy of temperature quenching of Eu(III)* PL with increase in Eu(fod)$_3$ concentration (Fig. 5). Thus, factors leading to a decrease in association of Eu(fod)$_3$ in xylene solutions increase the yield of Eu(fod)$_3$* luminescence.

## LITERATURE CITED

1. V. A. Belyakov, R. F. Vasil'ev, and G. F. Fedorova, Izv. Akad. Nauk SSSR, Ser. Fiz., **22**, No. 8, 1325 (1968).
2. R. F. Vasil'ev and D. M. Nalbandyan, Theory and Practice of Liquid-Phase Oxidation [in Russian], Nauka, Moscow (1974), p. 255.
3. P. D. Wildes and E. H. White, J. Am. Chem. Soc., **93**, No. 23, 6286 (1971).
4. F. McCapra and D. Watmore, Tetrahedron Lett., **23**, No. 49, 5225 (1982).
5. S. S. Ostakhov, G. L. Sharipov, A. I. Voloshin, et al., Dokl. Akad. Nauk SSSR, **287**, No. 5, 1165 (1986).
6. V. L. Ermolaev, E. B. Sveshnikova, and T. A. Shakhverdov, Usp. Khim., **45**, No. 10, 1753 (1976).
7. V. L. Ermolaev, E. B. Sveshnikova, and T. A. Shakhverdov, Radiationless Transfer of Electronic—Excitation Energy [in Russian], Nauka, Leningrad (1977), p. 311.
8. K. R. Korecky, J. E. Filby, C. Mumford, et al., Can. J. Chem., **53**, No. 8, 1103 (1975).
9. G. W. Shuster, N. J. Turro, H.-G. Steinmetzer, et al., J. Am. Chem. Soc., **97**, No. 24, 7110 (1975).
10. G. A. Tolstikov, G. L. Sharipov, A. I. Voloshin, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 787 (1986).
11. W. Adam, The Chemistry of Functional Groups: Peroxides, S. Patai (ed.), Wiley, New York (1983), p. 829.
12. N. J. Turro, D. Brewer, W. Farneth, and V. Ramamurthy, Nouv. J. Chem., **2**, No. 7, 85 (1978).
13. D. J. Raber, C. M. Janks, M. D. Johnston, and N. K. Raber, J. Am. Chem. Soc., **102**, No. 21, 6591 (1980).
14. V. L. Levshin, Photoluminescence of Liquid and Solid Substances [in Russian], Tekhni. Lit., Moscow—Leningrad (1951).