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# Chemiluminescence in visible and infrared spectral regions and quantum chain reactions upon thermal and photochemical decomposition of adamantylideneadamantane-1,2-dioxetane in the presence of chelates $Pr(dpm)_3$ and $Pr(fod)_3$

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## Abstract

Catalysis of adamantylideneadamantane-1,2-dioxetane (AAD) decomposition in the presence of chelates $Pr(fod)_3$ or $Pr(dpm)_3$ proceeds through the formation of the complex AAD·$Pr(fod)_3$ or AAD·$Pr(dpm)_3$, respectively. The rate constants ($k_2$) of AAD decomposition in the AAD·$Pr(fod)_3$ complex and stability constants ($K$) of the complex have been determined by the chemiluminescence method. The Arrhenius parameters of AAD decomposition in AAD·$Pr(fod)_3$ ($\lg A = 12 \pm 1.2$ and $E_a = 26 \pm 3$ kcal mol$^{-1}$) and thermodynamical parameters of the formation of AAD·$Pr(fod)_3$ ($\Delta H = 7.6 \pm 2.8$ kcal mol$^{-1}$ and $\Delta S = 29 \pm 10$ kcal degree mol$^{-1}$) have been calculated from the temperature dependencies of $k_2$ and $K$. In the case of $Pr(dpm)_3$ the parameters $K$ and $k_2$ could not be obtained since the complex decomposed at the conditions of kinetical experiments, although an estimation of the activation energy of AAD·$Pr(dpm)_3$ decomposition gave $E_a = 25 \pm 2$ kcal mol$^{-1}$. Upon decomposition of AAD·$Pr(fod)_3$ or AAD·$Pr(dpm)_3$ excitation of $Pr^{3+}$ occurs. In the case of AAD·$Pr(fod)_3$ the efficiency of excitation was estimated to be $\phi_{Pr^*} \leq 10\%$. The reaction is accompanied by chemiluminescence in visible and infrared regions due to radiative transitions from $^3P_1$, $^3P_0$ and $^1D_2$ levels of $Pr^{3+}$. Photochemical decomposition of AAD initiated by $Pr(fod)_3$* is accompanied by quantum chain reaction, the quantum yield of photolysis is $\phi_{max} = 3.6 \pm 1.2$ mol Einstein$^{-1}$. The branched quantum chain reaction is observed on thermal decomposition of AAD in the presence of an excess amount of $Pr(fod)_3$. Branching of the chain may be realized through the quenching of $Pr(fod)_3^*$ where $Pr^{3+}$ is in the $^3P_0$ or $^3P_1$- excited states by the AAD·$Pr(fod)_3$ complex with the preservation of excitation energy of $Pr^{3+}$ in lower lying $^1D_2$-state. Energy transfer on the $Pr(fod)_3$·AAD complex results in the decomposition of AAD with excitation of $Pr^{3+}$ into $^3P_1$, $^3P_0$ or $^1D_2$ state. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Chemiluminescence; Quantum chain reactions; Dioxetane; Praseodymium chelates; Photolysis

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## 1. Introduction

Dioxetanes are energy-rich four-membered cyclic peroxides that readily decompose to give carbonyl products that are formed with high yields in singlet and triplet excited states [1–3]. Usually with dioxetanes the yield of triplet excitation is 10–100 times higher than that for singlet excitation [1–3]. Decomposition is accompanied by chemiluminescence (CL). The interest for four-membered peroxides is dictated by their participation as key intermediates in bright bio- and chemiluminescent reactions [4,5]. At present dioxetanes found application as chemiluminescent labels in bioanalytical chemistry [6]. Energy of excited carbonyl products formed upon dioxetane decomposition may be transferred to the energy acceptor such as organic luminophore or coordinationally saturated metal complex, such as $Eu(TTA)_3$·Phen. CL enhancement in that case is realized through energy transfer and is not accompanied by the acceleration of the decomposition rate of peroxide [7–10].

Dioxetane decomposition is catalyzed by metal complexes and salts. The reaction may be accompanied by CL of the catalyst. It is established that catalysis by transition metal compounds proceed though the ‘dark’ pathway, i.e. without formation of excited products [11–14]. In contrast to transition metal compounds lanthanide ion complexes may efficiently accept triplet excitation energy [15–20] and re-emit it in visible and infrared spectral regions in catalytic reactions with dioxetane [21–23].

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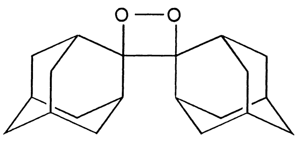
Efficiency of excitation and CL of catalyst is determined by the following conditions: (i) the availability of the luminescent levels of catalyst to which the excitation energy released upon dioxetane decomposition can be transferred; (ii) the value of luminescence yield of the catalyst molecule.

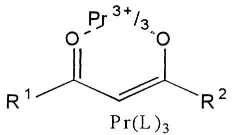
Decomposition of peroxide in the coordination sphere of metal ion results in the formation of dynamically non-equilibrium state of metal complex ('hot' complex). The formed 'hot' complex has a CL spectrum that differs from the photoluminescence (PL) spectrum of the equilibrium complex [24]. This indicates that 'hot' complex cannot be reached through photo- but only through chemiexcitation. The cases when spectra of CL and PL do not coincide are rare enough, but intriguing since they underline the specificity of the chemical generation of excited states and can bring light on the intimate details of chemiexcitation.

Generation of excited products at thermal and photochemical decomposition [25–34] of dioxetanes results in quantum chain processes emerging due to the reaction between triplet-excited ketone and dioxetane [35–40]. Quantum chain reactions may also take place upon dioxetane decomposition in the presence of organic activators or metal compounds [41,42], in the latter case branched QCR may occur [43–45].

Usually the investigations concerning PL and CL of rare earth ion complexes in solutions are conducted with brightly luminescent $Eu^{3+}$ and $Tb^{3+}$ compounds. The $Pr^{3+}$ compounds that have ff-luminescence consisting of a large number of lines [46–50] but have extremely low luminescence yield in solutions [50,51] are rarely used in such studies and information considering their chemiluminescent properties is absent. This paper presents the results of the investigation of kinetics, CL and photolysis of a model compound adamantylideneadamantane-1,2-dioxetane (AAD) in the presence of chelates the $Pr(fod)_3$ and $Pr(dpm)_3$.



AAD



$Pr(L)_3$
L = (fod): $R^1 = {}^tBu$, $R^2 = C_3F_7$
L = (dpm): $R^1 = R^2 = {}^tBu$

## 2. Experimental

### 2.1. Materials

AAD was synthesized as in [53]. β-Diketonates $Pr(L)_3$ were purified by sublimation and were dried before use at 70°C under vacuum. Toluene that was dried by boiling over metallic sodium and distilled was used as a solvent in all experiments.

### 2.2. Experimental methods

Kinetical and chemiluminescent experiments were carried out on home-built equipment ('CL box') described elsewhere [54,55] calibrated in absolute units photon $ml^{-1}\,s^{-1}$ using a Hastings–Weber scintillation cocktail [56]. The kinetics of AAD decomposition was followed by registration of CL decay. The kinetics of CL decay in the presence of $Pr(fod)_3$ and $Pr(dpm)_3$ obeyed the first-order reaction law in the whole concentration range of chelates studied and to the conversion level of 90% of dioxetane. Kinetical measurements were carried out in the temperature range 80–93°C, at $[AAD] = 10^{-3}$ M and $[Pr(fod)_3]$ $2.5 \times 10^{-3} \div 5.6 \times 10^{-2}$ M. For $Pr(dpm)_3$ the conditions were 95–108°C, $[AAD] = 10^{-3}$ M and $[Pr(dpm)_3]$ $7{\cdot}10^{-3} \div 1.5 \times 10^{-2}$ M.

The dependencies of CL intensity of AAD on the concentration of chelates were registered at the conditions when the decomposition of AAD during the experiment could be neglected (observed rate of dioxetane decomposition was less than $10^{-5}\,s^{-1}$). The dependencies were registered at relatively low temperatures compared with the kinetical measurements so that no CL intensity decay could be observed during the experiment (the CL intensity was at a constant level throughout the experiment). The conversion level of AAD during these experiments was less than 1%. Activation energy of AAD CL was calculated by equation $\ln I = \mathrm{const} - E_a/RT$, where $I$ – CL intensity at temperature $T$. The AAD CL intensity was measured in the temperature range 60–75°C, at $[AAD] = 10^{-3}$ M and $[Pr(fod)_3]$ $10^{-3} \div 7.5 \times 10^{-2}$ M. For $Pr(dpm)_3$ these experiments were conducted at 65–90°C, $[AAD] = 10^{-3}$ M and $[Pr(dpm)_3]$ $5 \times 10^{-3}$–$3 \times 10^{-2}$ M.

PL spectra were recorded on spectrofluorimeter MPF-4 'Hitachi,' absorption spectra – on spectrophotometer 'Specord M-40.' CL spectra in visible and infrared were recorded on home-built equipment described elsewhere [2,54,55]. PMR spectra were obtained on 'Bruker-AM-300' using TMS as an internal standard in toluene-$d_8$, at room temperature with $[AAD] = 10^{-2}$ M and $[Pr(fod)_3]$ $5 \times 10^{-2}$–$2 \times 10^{-1}$ M.

Photolysis of AAD in the presence of $Pr(fod)_3$ was carried out in a cell compartment of a spectrofluorimeter MPF-4 'Hitachi' by irradiation with light at wavelength $\lambda = 450$ nm. The light intensity was determined by ferrioxalate actinometer [57]. The volume of irradiated solution was 4 ml, the intensity of light $I = 2.8{\cdot}10^{14}$ photon $s^{-1}$. AAD concentration in the course of photolysis was determined by CL method [34]. Photolysis of AAD in the presence of $Pr(fod)_3$ was carried out at 20°C, at $[Pr(fod)_3] = 10^{-1}$ M and [AAD] $10^{-2} \div 8 \times 10^{-2}$ M. Photolysis was carried out for 11–12 h until the conversion of AAD reached 5–15%. Photolysis quantum yields were calculated from the initial part of the kinetical curve by equation $\Phi = \Delta[AAD]/I \times \Delta t$, where $\Phi$ – quantum yield of AAD photolysis, $\Delta[AAD]$ is the change of the AAD concentration at the time $\Delta t$, upon irradiation with light of intensity $I$.

## 3. Discussion

### *3.1. Catalysis of AAD decomposition by Pr(fod)$_3$*

AAD in toluene solution decomposes to give two molecules of adamantanone (Ad=O), which are formed in ground and excited (triplet or singlet) state Eq. (1)[53]. Activation energy for decomposition of the alkyl- and alkoxy-substituted dioxetanes is ca. 25 kcal mol$^{-1}$ [1]. The presence of bulky, i.e. adamantyl substituents in the peroxide ring results in substantial increase of the activation energy by ca. 5–10 kcal mol [53,58–60]. Activation energy of AAD decomposition ($\lg A = 14.1$, $E_a = 34$ kcal mol$^{-1}$) characterizes it as an extraordinarily stable compound among the dioxetanes [53]. CL upon AAD decomposition is due to radiative deactivation of singlet-excited adamantanone with emission maximum at $\lambda_{\max} = 420$ nm. Fluorescence and phosphorescence quantum yields for adamantanone are $\phi_{\mathrm{fl}} = 0.015$ and $\phi_{\mathrm{P}} = 4{\cdot}10^{-5}$ [54], respectively.

$$\mathrm{AAD} \xrightarrow{k_1} 1.83\,\mathrm{Ad} = \mathrm{O} + 0.15\,\mathrm{Ad} = \mathrm{O_T^*} + 0.02\,\mathrm{Ad} = \mathrm{O_s^*} \qquad (1)$$

Pr(fod)$_3$ added to AAD solution accelerates the rate of AAD CL decay more than $10^2$ times (Fig. 1) and enhances the CL intensity (Fig. 2). Moreover, in the CL spectrum new emission bands appear that can be attributed to the radiative ff-transitions of Pr$^{3+}$ (Figs. 3 and 4).

The characteristic coordination number for rare earth (RE) ions is known to be 8 or 9. Only six coordination sites of Pr$^{3+}$ are occupied in Pr(fod)$_3$ and thus Pr(fod)$_3$ readily forms complexes with compounds that have oxygen atoms [61]. Obviously in toluene solution Pr(fod)$_3$ forms a complex with AAD with stability constant $K$, where the Pr$^{3+}$ ion is coordinated by the oxygen atoms of peroxide Eq. (2):

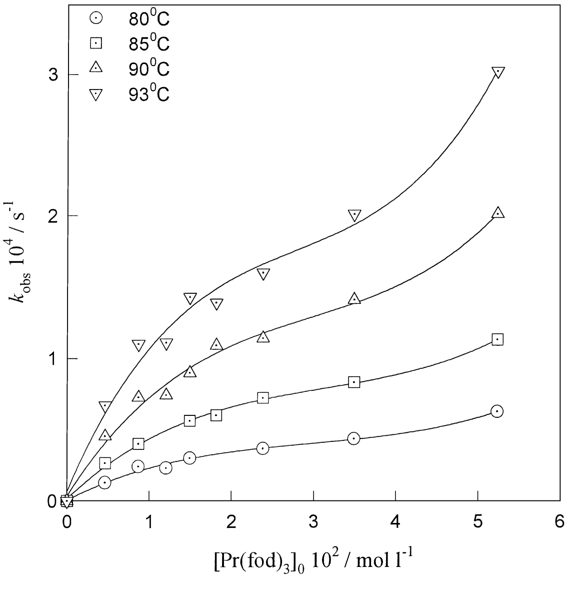


Fig. 1. Dependence of $k_{\mathrm{obs}}$ of CL decay on the concentration of Pr(fod)$_3$ upon thermolysis of $10^{-3}$ M AAD in toluene.

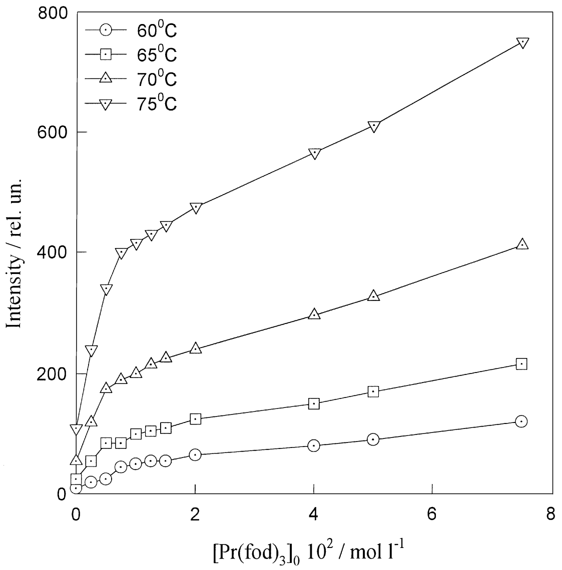


Fig. 2. Dependence of intensity of CL upon thermolysis of $10^{-3}$ M AAD in toluene on the concentration of Pr(fod)$_3$.

$$\mathrm{AAD} + \mathrm{Pr(fod)_3} \overset{K}{\rightleftarrows} \mathrm{AAD} \cdot \mathrm{Pr(fod)_3} \qquad (2)$$

Weakening of the peroxide bond in AAD induced by complex formation facilitates its decomposition Eq. (3). The population of the excited levels of Pr$^{3+}$ occurs with the efficiency $\phi_{\mathrm{Pr^*}}$ upon peroxide decomposition in the complex since sufficient energy is released for that process [62,63] (Eq. (3), Fig. 5). The excited complex [Pr(fod)$_3{}^*$· 2Ad=O] deactivates either with the emission of CL Eq. (4) or non-radiatively (not shown).

$$\mathrm{AAD} \cdot \mathrm{Pr(fod)_3} \xrightarrow{k_2} \phi_{\mathrm{Pr^*}}[\mathrm{Pr(fod)_3^*} \cdot 2\,\mathrm{Ad} = \mathrm{O}] + (1 - \phi_{\mathrm{Pr^*}})[\mathrm{Pr(fod)_3} \cdot 2\,\mathrm{Ad} = \mathrm{O}] \qquad (3)$$

$$[\mathrm{Pr(fod)_3^*} \cdot 2\,\mathrm{Ad} = \mathrm{O}] \rightarrow [\mathrm{Pr(fod)_3} \cdot 2\,\mathrm{Ad} = \mathrm{O}] + h\nu \qquad (4)$$

The chelate may also be excited by intermolecular energy transfer from triplet-excited adamantanone formed in reaction (1) with subsequent emission of CL Eqs. (5) and (6). The presence of the emission bands of Pr$^{3+}$ in the CL spectrum of AAD–Pr(fod)$_3$ system evidences the excitation of Pr$^{3+}$ in the reactions (3) or (5).

$$\mathrm{Ad{=}O_T^*} + \mathrm{Pr(fod)_3} \rightarrow \mathrm{Ad{=}O} + \mathrm{Pr(fod)_3^*} \qquad (5)$$

$$\mathrm{Pr(fod)_3^*} \rightarrow \mathrm{Pr(fod)_3} + h\nu \qquad (6)$$

Included into the scheme Eqs. (1)–(6) should be the reactions of complex formation between Pr(fod)$_3$ and product of AAD decomposition – adamantanone Eq. (7) or with

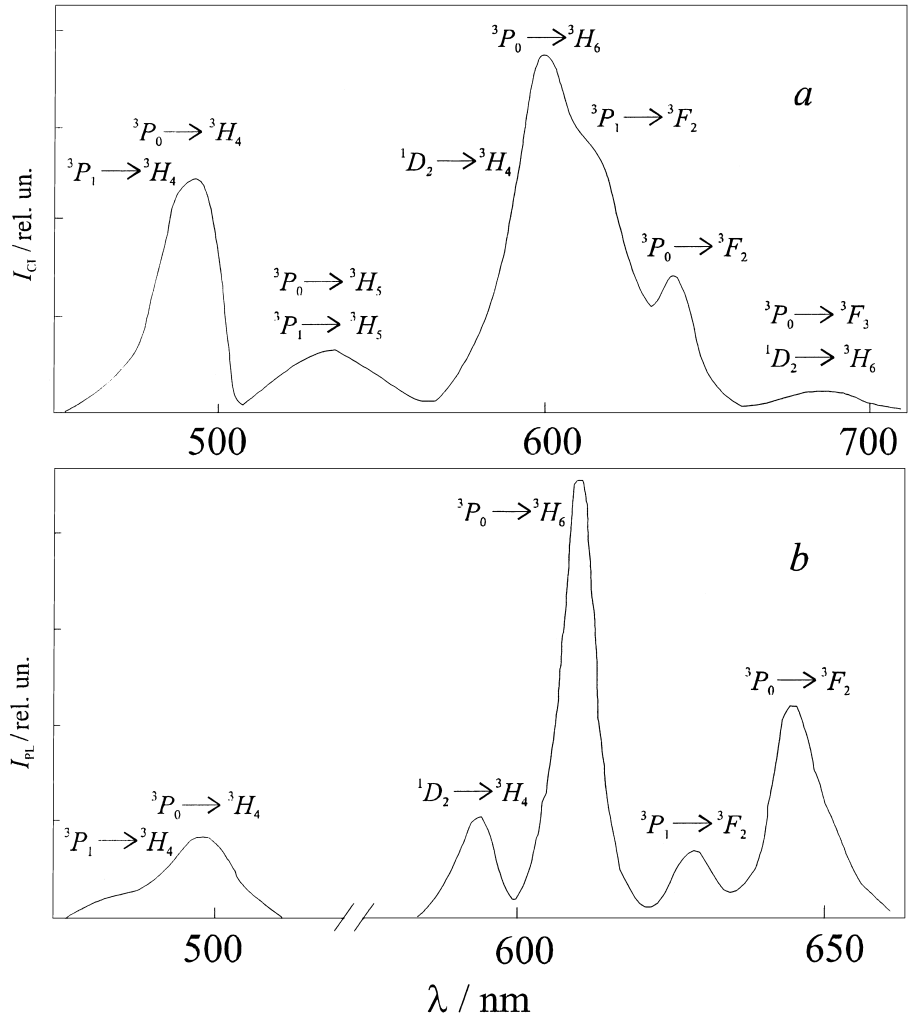


Fig. 3. Pl and CL spectra. (a) CL spectra of $10^{-2}$ M AAD in the presence of $7{\cdot}10^{-2}$ M Pr(fod)$_3$ at 90°C in toluene (spectral slit $\Delta\lambda = 7$ nm). (b) PL spectra of $10^{-2}$ M Pr(fod)$_3$ in $d_8$-toluene at room temperature, $\lambda_{ex} = 370$ nm (spectral slit $\Delta\lambda = 5$ nm).

water that comes with solvent and reagents. Thus in order to obtain correct kinetical results one should use an excess amount of Pr(fod)$_3$ relative to AAD and the solvents and reagents to be used should be thoroughly dried.

$$\mathrm{Ad{=}O} + \mathrm{Pr(fod)_3} \rightleftarrows \mathrm{Ad{=}O} \cdot \mathrm{Pr(fod)_3} \qquad (7)$$

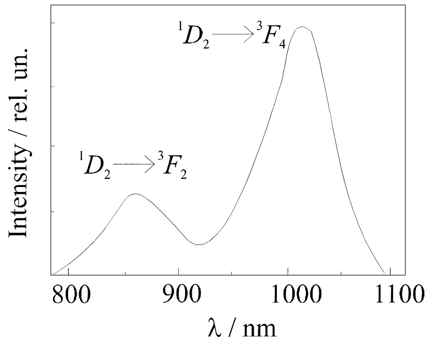


Fig. 4. CL spectrum in infrared of $10^{-2}$ M AAD in the presence of $7 \times 10^{-2}$ M Pr(fod)$_3$ at 90°C in toluene (spectral slit $\Delta\lambda = 15$ nm).

The kinetical measurements of AAD decomposition in the presence of Pr(fod)$_3$ were carried out in order to determine the activation parameters of reaction (3) and thermodynamical parameters of AAD·Pr(fod)$_3$ complex formation. The intensity of CL is proportional to the total concentration of AAD and the rate of its decay is proportional to the rate of consumption of AAD, i.e. $I \sim \mathrm{d[AAD]/d}t = k_{obs}[\mathrm{AAD}]$. According to Eqs. (1) and (3) the dioxetane is consumed in two directions: decomposition of the uncomplexed dioxetane with rate constant $k_1$ and decomposition of AAD·Pr(fod)$_3$ complex with rate constant $k_2$. Analysis of kinetical scheme Eqs. (1)–(3) taking into account that $[\mathrm{Pr(fod)_3}]_0 > [\mathrm{AAD}]$, where $[\mathrm{Pr(fod)_3}]_0$ – is the total amount of chelate Pr(fod)$_3$ present in the system, results in the following equation for $k_{obs}$:

$$k_{obs} = (k_1 + k_2 \cdot K \cdot [\mathrm{Pr(fod)_3}]_0) \cdot (1 + K \cdot [\mathrm{Pr(fod)_3}]_0)^{-1} \qquad (8)$$

In order to determine $k_2$ and $K$, Eq. (8) can be rewritten in the following form:

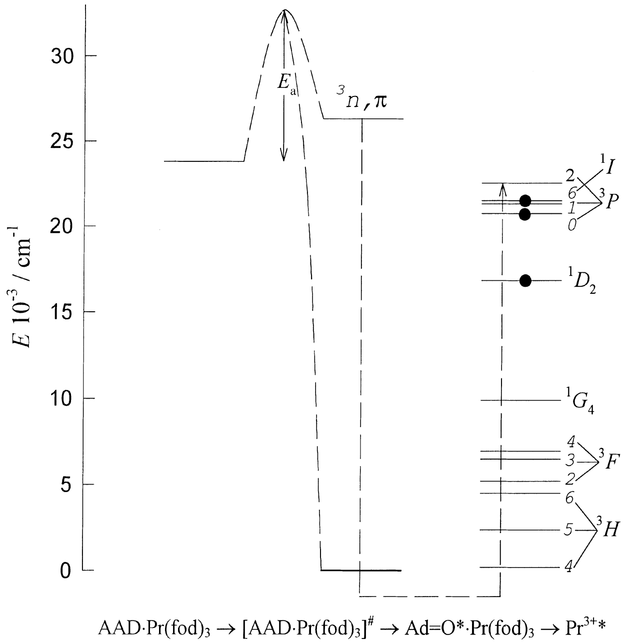


Fig. 5. Energy scheme for AAD decomposition in the complex Pr(fod)$_3$·AAD. The energy of the triplet adamantanone $E_T = 75.2$ kcal mol$^{-1}$ [10]; the enthalpy of decomposition of 1,2-dioxetane is $\Delta H \approx 68$ kcal mol$^{-1}$ [62]. Photo- and CL are observed from the Pr$^{3+}$ levels marked by (•).

$$(k_{obs} - k_1)^{-1} = (k_2 - k_1)^{-1} + \{(k_2 - k_1) \cdot K \cdot [\mathrm{Pr(fod)_3}]_0\}^{-1} \qquad (9)$$

Eq. (9) was used for the calculation of $k_2$ and $K$. The rate constants $k_2$ were determined from the intercept cut by the line on the $(k_{obs} - k_1)^{-1}$ axis in the $[\mathrm{Pr(fod)_3}]_0^{-1}$–$(k_{obs} - k_1)^{-1}$ coordinates, and the stability constants $K$ were determined from the tangent of the slope. The following Arrhenius parameters of AAD decomposition determined in our laboratory were used for the calculation of $k_1$ : lg$A$ = 14.2, $E_a$ = 35.1 kcal mol$^{-1}$.

According to Eq. (8) the dependence of $k_{obs}$ upon $[\mathrm{Pr(fod)_3}]_0$, should be the curve that originates from the value of $k_1$ in the absence of Pr(fod)$_3$ and reaches the value $k_2$ with the increase of $[\mathrm{Pr(fod)_3}]_0$. The dependence of $k_{obs}$ upon $[\mathrm{Pr(fod)_3}]_0$ indeed reaches saturation but than at $[\mathrm{Pr(fod)_3}]_0 > 0.035$ M it grows up again (Fig. 1). This unexpected increase of $k_{obs}$ at $[\mathrm{Pr(fod)_3}]_0 > 0.035$ M cannot be explained by the formation of complexes of the composition AAD·2Pr(fod)$_3$ since we could not find evidence for formation of such species in the PMR study of complex formation in the AAD–Pr(fod)$_3$ system. Apparently at high Pr(fod)$_3$ concentrations additional processes emerge that facilitate the catalyzed decomposition of AAD. Regarding the high instability of dioxetanes the possible route for an effective decomposition of dioxetane at $[\mathrm{Pr(fod)_3}]_0 > 3.5 \cdot 10^{-2}$ M may be the photocatalytic decomposition of AAD initiated by Pr(fod)$_3$ in the excited state formed in reaction (3).

The scheme for AAD decomposition including Eqs. (1)–(6) is applicable in the Pr(fod)$_3$ concentration range (5–35) × $10^{-3}$ M. Indeed in that range the dependence of $k_{obs}$ – $[\mathrm{Pr(fod)_3}]_0$ is linear in the coordinates of Eq. (9). The rate constants $k_2$ and stability constants $K$ were determined from dependence $[\mathrm{Pr(fod)_3}]^{-1}$ – $(k_{obs} - k_1)^{-1}$ according to Eq. (9) in the range $[\mathrm{Pr(fod)_3}]_0 = (5 \div 35) \times 10^{-3}$ M (Table 1).

Complex AAD·Pr(fod)$_3$ is formed in endothermical reaction due to the positive entropy change (Table 1). Enthalpy change upon complex formation is difference between the energy that is required for a desolvation of Pr(fod)$_3$ (total or a partial) and the energy that is released in interaction of chelate and peroxide. The thermodynamical parameters obtained indicate that Pr(fod)$_3$ is solvated by toluene molecules. The dioxetane molecule that has bulky adamantyl substituents expels the toluene molecules from inner coordination sphere of Pr(fod)$_3$ upon complex formation and that results in a positive entropy change. Large positive entropy changes were observed earlier at complex formation between Pr(fod)$_3$ and substituted pyridines in benzene [61].

### *3.2. Luminescence spectra of Pr(fod)$_3$ upon photo- and chemiexcitation. Luminescence from chemically generated non-equilibrium complex*

Upon excitation of Pr$^{3+}$ in crystals and glasses into its ff-absorption bands the PL of Pr$^{3+}$ is observed from the $^3P_1$, $^3P_0$, $^1D_2$ levels in visible and infrared [46–48]. In solutions excitation of Pr$^{3+}$ into fd-absorption bands leads to the effective 5d–4f luminescence of Pr$^{3+}$ in the UV with ca. unit quantum efficiency [51,52]. In solutions the quantum yield of ff-luminescence of Pr$^{3+}$ compounds is extremely small [50,51]. Indeed the luminescence quantum yield of

Table 1
Rate constants of AAD decomposition in the complex AAD·Pr(fod)$_3$ ($k_2$) and stability constants of the AAD·Pr(fod)$_3$ complex ($K$) at different temperatures. Activation parameters of AAD decomposition in AAD·Pr(fod)$_3$ ($E_a$, lg$A$) and thermodynamical parameters of complex AAD·Pr(fod)$_3$ formation ($\Delta H$, $\Delta S$). All values calculated from the rate of AAD CL decay in the presence of Pr(fod)$_3$ Fig. 1

| $T$ (K) | $k_2 \times 10^4$ (s$^{-1}$) | $E_a$ (kcal mol$^{-1}$) | log$A$ | $K$ (l mol$^{-1}$) | $\Delta H$ (kcal mol$^{-1}$) | $\Delta S$ (cal mol$^{-1}$ deg$^{-1}$) |
|---|---|---|---|---|---|---|
| 353 | 0.66 | 26 | 12 | 53 | 7.6 | 29 |
| 358 | 1.2 | | | 63 | | |
| 363 | 1.8 | | | 71 | | |
| 366 | 2.5 | | | 79 | | |

Note: Errors for determination of $k_2$, $E_a$, lg$A$ are 15%; for determination of $K$, $\Delta H$, $\Delta S$ are 30%.

$Pr(fod)_3$ upon excitation either into ligand or ion absorption bands is $\phi_{Pr} < 10^{-4}$ at 20°C.

Notwithstanding that the quantum yield of adamantanone fluorescence is significantly higher than that of $Pr(fod)_3$, the addition of $Pr(fod)_3$ to AAD solution results in the enhancement of CL intensity more than 10 times with complete change of CL spectrum in which the ff-emission bands of $Pr^{3+}$ appear (Figs. 2–4). The similar character of the changes of $k_{obs}$ (Fig. 1) and intensity of CL (Fig. 2) upon $[Pr(fod)_3]_0$ demonstrates the direct connection between the 'light' steps and catalysis of the AAD decomposition in the presence of $Pr(fod)_3$. The enhancement of CL intensity at $[Pr(fod)_3]_0 > 3.5{\cdot}10^{-2}$ M reflects the complicated processes where an additional channel for formation of $Pr(fod)_3$ in excited state emerges.

$Pr^{3+}$ may get excited directly on decomposition of dioxetane in $Pr(fod)_3{\cdot}AAD$ complex Eq. (3) or by intermolecular energy transfer from excited adamantanone Eq. (5). The step responsible for the chemiexcitation of $Pr(fod)_3$ was revealed using adamantanone as a competitor with AAD in the complex formation reaction with the chelate. When adamantanone (up to $10^{-1}$ M) is present in the solution containing chelate $Pr(fod)_3$ ($3{\cdot}10^{-2}$ M) and AAD ($10^{-3}$ M) the CL is quenched to the level of CL emission in the absence of $Pr(fod)_3$ with complete disappearance of $Pr^{3+}$ emission bands in the CL spectrum. Obviously the adamantanone decreases the concentration of $AAD{\cdot}Pr(fod)_3$ by binding $Pr(fod)_3$ in the complex $Pr(fod)_3{\cdot}n\text{Ad=O}$ ($n = 1$ or 2) according to Eq. (7) and thus quenches $Pr^{3+}$ CL. The main pathway leading to the excitation of $Pr^{3+}$ is then AAD decomposition in the inner coordination sphere of $Pr^{3+}$ in the complex $AAD{\cdot}Pr(fod)_3$ followed by intracomplex energy transfer from excited adamantanone to $Pr^{3+}$ Eq. (3). Upon AAD decomposition the triplet-excited adamantanone is formed in preference to singlet Eq. (1). Evidently, in the catalytic act of AAD decomposition Eq. (3), the excitation is localized mainly on the $^3n, \pi^*$ – level of adamantanone, whose deactivation occurs by intersystem crossing $T_1 \rightarrow S_0$, or by energy transfer to the excited f-levels of $Pr^{3+}$ (Fig. 5).

An estimation of the excitation yield of $Pr^{3+}$ $\phi_{Pr^*}$ upon AAD decomposition by equation $\phi_{Pr^*} = I{\cdot}(\phi_{Pr}{\cdot}k_2{\cdot}[AAD{\cdot}Pr(fod)_3])^{-1}$ (where $I$ – absolute CL intensity, $\phi_{Pr}$ – PL yield of $Pr(fod)_3$) made from the measurements of absolute CL intensity and based on the assumption that $Pr^{3+}$ is excited only in the reaction (3), leads to the value $\phi_{Pr^*} \leq 10\%$. The high excitation yield of $Pr^{3+}$ $\phi_{Pr^*}$ Eq. (3) close to that of triplet-excited adamantanone Eq. (1) evidences the high efficiency of energy transfer from triplet adamantanone to $Pr^{3+}$ ion in the complex $[\text{Ad=O}{\cdot}Pr(fod)_3{\cdot}\text{Ad=O}^*]$, formed immediately after AAD decomposition.

The assignment of bands in the CL spectrum of AAD–$Pr(fod)_3$ system was made from a comparison of the energy levels of the $Pr^{3+}$ aqua ion (Fig. 5) [63], and the absorption and PL (Fig. 3(b)) spectra of $Pr(fod)_3$. Excitation of $Pr(fod)_3$ in the ligand absorption band ($\lambda = 370$ nm) or in the ff-absorption band of $Pr^{3+}$ ($^3H_4 \rightarrow {}^3P_2$ transition, $\lambda =$ 450 nm) leads to extremely weak $Pr^{3+}$ PL with $\lambda_{max} = 480$, 495, 595, 610, 625, 645 (±5) nm caused by radiative transitions from $^3P_1, {}^3P_0, {}^1D_2$ levels (Fig. 3(b)). The main part of the $Pr^{3+}$ PL is observed not from the resonant $^1D_2$, but from a higher lying $^3P_0$ level [50]. It should be noted that adamantanone and AAD only slightly enhance the PL of $Pr(fod)_3$.

In the CL spectrum of the AAD–$Pr(fod)_3$ system maxima are observed at $\lambda_{max} = 480$, 490, 535, 590, 605, 620, 640, 690 (±5) and 850, 1000 (±20) nm, corresponding to the transitions originating from the $^3P_1, {}^3P_0$ and $^1D_2$ levels of $Pr^{3+}$ (Figs. 3 and 4). The intensity of emission in IR region at 1000 nm ($^1D_2 \rightarrow {}^3F_4$ transition) is comparable with that in visible region at 605 nm ($^3P_0 \rightarrow {}^3H_4$ transition), taking into account the spectral sensitivity of the equipment used. That demonstrates the close efficiencies of the population of $^3P_0$ and $^1D_2$ excited states of $Pr^{3+}$ in reaction (3). As in PL the main part of the $Pr^{3+}$ CL originates from the $^3P_0$ level while in IR the bands are due to radiative transitions from the $^1D_2$ level. However, a redistribution of band intensities occurs in the $Pr^{3+}$ CL spectrum compared with that of PL and new maxima at 535 and 690 nm appear (Fig. 3), that are not recorded in the PL spectra although the sensitivities of the CL and PL spectral measuring equipment in the spectral region studied are identical.

We think that the emitters of the observed CL are the 'hot' complexes $[Pr(fod)_3{\cdot}n\text{Ad=O}]^*$ (where $n = 1$, 2) formed immediately after decomposition of dioxetane in the complex $AAD{\cdot}Pr(fod)_3$. We suppose that such complex has non-equilibrium geometry of coordination sphere caused by the relatively slow rate of relaxation of the bulky ligands from the inherited coordination sphere of $AAD{\cdot}Pr(fod)_3$ complex to the equilibrium geometry of $[Pr(fod)_3{\cdot}n\text{Ad=O}]^*$ complex. This rate should be comparable with the rate of deactivation of the excited state of $Pr^{3+}$, estimated to be ca. $10^6$ $s^{-1}$ [64,65]. We think that the non-equilibrium character of the coordination sphere of the $[Pr(fod)_3{\cdot}n\text{Ad=O}]^*$ complex results in the observed differences in the CL and PL spectra of $Pr^{3+}$. Similar differences between PL and CL spectra were observed previously in the AAD–$Eu(fod)_3$ system [24].

It seems that the photophysical properties of such chemically generated non-equilibrium excited complex $[Pr(fod)_3{\cdot}n\text{Ad=O}]^*$, viz. quantum yield and emission spectrum, differ from that of the chelate $Pr(fod)_3$ or $[Pr(fod)_3{\cdot}n\text{Ad=O}]$, a fact which is responsible for the observed $Pr^{3+}$ CL intensity and redistribution of luminescence intensity of the bands in the CL spectrum compared with PL spectrum of $Pr^{3+}$.

### *3.3. Decomposition and CL of AAD in the presence of the chelate $Pr(dpm)_3$*

In the presence of coordination unsaturated chelate $Pr(dpm)_3$ the scheme for AAD decomposition is the same as in the $Pr(fod)_3$–AAD system (Figs. 1–7). The catalysis is

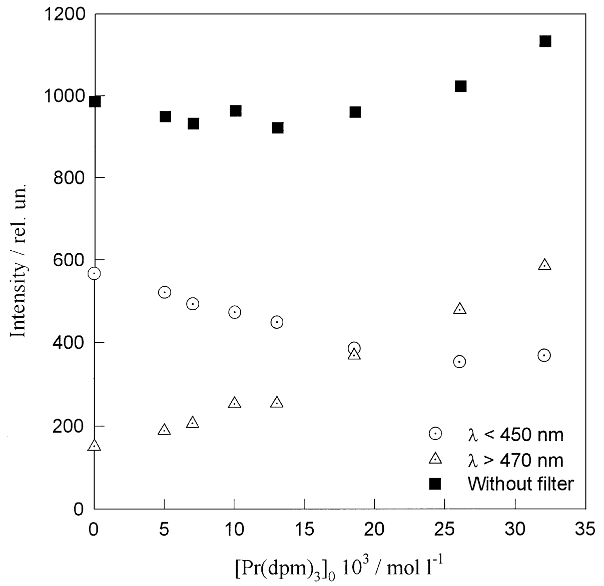


Fig. 6. Dependence of intensity of CL upon thermolysis of $10^{-3}$ M AAD at 90°C in toluene on $\mathrm{Pr(dpm)_3}$ concentration in different spectral regions.

rather inefficient and the observed decomposition rate of AAD ($k_{\mathrm{obs}}$) in the presence of $\mathrm{Pr(dpm)_3}$ does not exceed $2 \times 10^{-5}$ s$^{-1}$. Inefficiency of the catalysis of the reaction by $\mathrm{Pr(dpm)_3}$ may be explained by weak coordination ability of $\mathrm{Pr(dpm)_3}$ compared with $\mathrm{Pr(fod)_3}$ [61]. We could not obtain reproducible results on investigation of the catalysis of AAD decomposition by $\mathrm{Pr(dpm)_3}$. The reason for this may be the decomposition of $\mathrm{Pr(dpm)_3}$ in toluene in the conditions of the kinetical experiments that required prolonged thermolysis (2–5 h) at high temperatures. Instability of chelate $\mathrm{Pr(dpm)_3}$ in benzene was mentioned elsewhere [61,66].

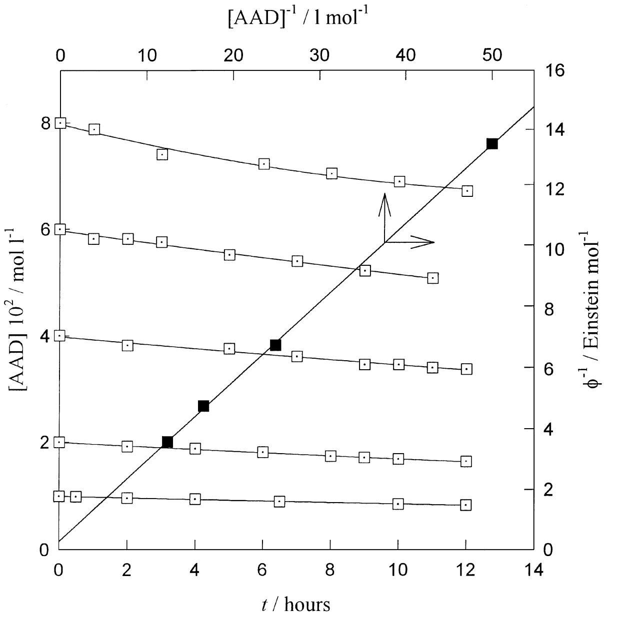


Fig. 7. Kinetics of photolysis of AAD in the presence of $10^{-1}$ M $\mathrm{Pr(fod)_3}$ in toluene at 20°C at different initial concentrations of AAD on irradiation with light $\lambda = 450$ nm (□). Determination of the maximum quantum yield from the kinetics of photo decomposition of AAD in the presence of $10^{-1}$ M $\mathrm{Pr(fod)_3}$ at different initial concentrations of AAD (■).

Intensity of CL of AAD is enhanced only slightly with the increase of $\mathrm{Pr(dpm)_3}$ concentration with the change of the spectral distribution of CL emission. The lowering of the CL intensity in the region <450 nm (adamantanone fluorescence) is accompanied by almost linear enhancement of the CL intensity in the region >470 nm ($\mathrm{Pr^{3+}}$ emission) (Fig. 6). CL of $\mathrm{Pr^{3+}}$ is due to the excitation of $\mathrm{Pr^{3+}}$ in the reaction of the catalytic decomposition of AAD in AAD·$\mathrm{Pr(dpm)_3}$ complex Eq. (3). The activation energy of CL in the region of $\mathrm{Pr^{3+}}$ emission lowers with the increase of $\mathrm{Pr(dpm)_3}$ concentration and is 25 ± 2 kcal mol$^{-1}$ as calculated from the temperature dependence of CL intensity. This value is comparable with that for AAD·$\mathrm{Pr(fod)_3}$ complex (Table 1). At the same time an activation energy of CL in the region of adamantanone fluorescence does not change with the concentration of $\mathrm{Pr(dpm)_3}$ and is 33 ± 2 kcal mol$^{-1}$; that result is close to the activation energy of AAD decomposition. The $\mathrm{Pr(dpm)_3}$ PL spectrum and quantum yield are similar to that of $\mathrm{Pr(fod)_3}$. The CL spectrum of AAD–$\mathrm{Pr(dpm)_3}$ coincided with that for AAD–$\mathrm{Pr(fod)_3}$ system. Addition of adamantanone to the AAD–$\mathrm{Pr(dpm)_3}$ system as in the case with $\mathrm{Pr(fod)_3}$ results in the lowering of $\mathrm{Pr^{3+}}$ CL that proves the excitation of $\mathrm{Pr^{3+}}$ through intracomplex energy transfer (Fig. 3). The difference between CL and PL spectra is explained as in the case of $\mathrm{Pr(fod)_3}$ by the emission of $\mathrm{Pr^{3+}}$ from a non-equilibrium complex.

### 3.4. Photolysis of AAD in the presence of $\mathrm{Pr(fod)_3}$

Dioxetanes readily decompose into two carbonyl products upon irradiation with UV or IR light [25–30]. Energy transfer from donor to the electronic-excited levels or vibration overtones of dioxetane also facilitates its decomposition [31–34]. In such systems sensitized decomposition of peroxide may undergo with the quantum yield >1 [41,42]. Taking into account that the dissipation of the excitation energy of lanthanide ions proceeds through vibration overtones of the surrounding molecules [64,65] we supposed that photocatalytic decomposition of dioxetane may be realized due to such energy transfer upon irradiation of solutions containing AAD and $\mathrm{Pr^{3+}}$ chelate. The investigation was carried out on AAD–$\mathrm{Pr(fod)_3}$ system.

Photolysis of AAD was carried out under irradiation into the $\mathrm{Pr^{3+}}$ absorption band at 450 nm ($^3\mathrm{H}_4 \rightarrow {}^3\mathrm{P}_2$ transition). Dioxetane does not absorb in that region so no direct photolysis of dioxetane may take place in the system in question. Photolysis scheme can be represented by reactions (10)–(16), where $\alpha$ is the excitation regeneration coefficient of $\mathrm{Pr^{3+}}$.

$$\mathrm{Pr(fod)_3} \xrightarrow{h\nu} \mathrm{Pr(fod)_3}^* \qquad (10)$$

$$\mathrm{Pr(fod)}_3^* \xrightarrow{k_\mathrm{d}} \mathrm{Pr(fod)}_3 + \Delta \tag{11}$$

$$\mathrm{AAD} + \mathrm{Pr(fod)}_3^* \overset{K^*}{\rightleftarrows} \mathrm{AAD} \cdot \mathrm{Pr(fod)}_3^* \tag{12}$$

$$\mathrm{Pr(fod)}_3^* + \mathrm{AAD} \cdot \mathrm{Pr(fod)}_3 \rightarrow \mathrm{Pr(fod)}_3 + \mathrm{AAD} \cdot \mathrm{Pr(fod)}_3^* \tag{13}$$

$$\mathrm{AAD} \cdot \mathrm{Pr(fod)}_3 \xrightarrow{h\nu} \mathrm{AAD.Pr(fod)}_3^* \tag{14}$$

$$\mathrm{AAD} \cdot \mathrm{Pr(fod)}_3^* \rightarrow \mathrm{AAD} \cdot \mathrm{Pr(fod)}_3 + \Delta \tag{15}$$

$$\begin{aligned}\mathrm{AAD.Pr(fod)}_3^* &\xrightarrow{k_\mathrm{et}} \alpha[\mathrm{Pr(fod)}_3{}^* \cdot 2\,\mathrm{Ad{=}O}] \\ &+ (1-\alpha)[\mathrm{Pr(fod)}_3 \cdot 2\,\mathrm{Ad{=}O}]\end{aligned} \tag{16}$$

The excited state of $\mathrm{Pr(fod)_3}$ is formed upon absorption of photon Eq. (10). Then $\mathrm{Pr(fod)}_3^*$ deactivates either non-radiative Eq. (11), forms complex with AAD Eq. (12) or is quenched by AAD·$\mathrm{Pr(fod)_3}$ complex Eq. (13). The path for radiative deactivation of $\mathrm{Pr(fod)}_3^*$ is not taken into account since the quantum yield of $\mathrm{Pr(fod)_3}$ luminescence is low. The excited $\mathrm{Pr(fod)}_3^*$ may be formed also upon direct absorption of light by AAD·$\mathrm{Pr(fod)_3}$ complex (Eq. (14)) since in the non-irradiated system AAD–$\mathrm{Pr(fod)_3}$ the equilibrium (2) takes place. An excited complex $\mathrm{Pr(fod)}_3^*$ formed in reactions (12)–(14) in its turn either dissociates Eq. (12) or deactivates through the energy transfer on vibration overtones of the ligand Eq. (15). Intracomplex energy transfer from $\mathrm{Pr}^{3+}$ in $\mathrm{Pr(fod)}_3^*$ to vibration overtones of AAD results in its decomposition Eq. (16).

Absorption of the photon of excitation light by $\mathrm{Pr}^{3+}$ results in the formation of the $^3\mathrm{P}_2$ state Eq. (10), that rapidly deactivates by non-radiative pathways to give lower lying excited states. Probably in photochemical reactions the complexes $\mathrm{Pr(fod)}_3^*$ take part where $\mathrm{Pr}^{3+}$ is in the excited $^3\mathrm{P}_1$ or $^3\mathrm{P}_0$ or $^1\mathrm{D}_2$ states, since from these rather long-living states the PL and CL of $\mathrm{Pr}^{3+}$ are observed. The kinetics of photolysis at different initial concentrations of AAD is shown on Fig. 7.

Reaction (13) can be neglected at the large concentration of dioxetane and the photolysis quantum yield is then given by Eq. (17):

$$\phi = k_\mathrm{et} \cdot K^* \cdot [\mathrm{AAD}] \cdot \{k_\mathrm{d} + (1-\alpha) \cdot (k_\mathrm{et} \cdot K^* \cdot [\mathrm{AAD}])\}^{-1} \tag{17}$$

From the dependence of observed quantum yield upon concentration of AAD in the coordinates $[\mathrm{AAD}]^{-1} - \phi^{-1}$ at $[\mathrm{AAD}]^{-1} = 0$, the maximum quantum yield in this system was determined to be $\phi_\mathrm{max} = 3.6 \pm 1.2\ \mathrm{mol\ Einstein}^{-1}$ (Fig. 7). Regeneration coefficient of $\mathrm{Pr(fod)}_3^*$ was calculated from the equation $\phi_\mathrm{max} = (1-\alpha)^{-1}$, is $0.7 \pm 0.2$. Tangent of the slope of the dependence $\phi^{-1}$upon $[\mathrm{AAD}]^{-1}$ equal to the value $k_\mathrm{d} \cdot (k_\mathrm{et} \cdot K^*)^{-1}$ is $0.26 \pm 0.03$. Taking into account that $k_\mathrm{d}$ is ca. $10^6\ \mathrm{s}^{-1}$ [64,65] we obtain the estimation of $k_\mathrm{et} \cdot K^* \approx 10^6 \div 10^7 \mathrm{l\ mol}^{-1}\ \mathrm{s}^{-1}$. This result is in accordance with the previously obtained for the system $\mathrm{Eu(fod)_3}$–AAD where $k_\mathrm{et} \cdot K^* = (2.2 \pm 0.5) \cdot 10^6\ \mathrm{l\ mol}^{-1}\ \mathrm{s}^{-1}$ [42].

The obtained value of quantum yield is higher than unit although it is obvious that absorption of photon by either $\mathrm{Pr(fod)_3}$ or AAD·$\mathrm{Pr(fod)_3}$ complex may lead to the decomposition of only one molecule of AAD. The result obtained shows that the regeneration of excited $\mathrm{Pr(fod)}_3^*$ in the $^3\mathrm{P}_1$, $^3\mathrm{P}_0$ or $^1\mathrm{D}_2$ states takes place in the system $\mathrm{Pr(fod)}_3^*$–AAD after the decomposition of AAD Eq. (16). Moreover, the formed complex $[\mathrm{Pr(fod)}_3^* \cdot 2\mathrm{Ad{=}O}]$ dissociates and may meet and react with another molecule of AAD or AAD·$\mathrm{Pr(fod)_3}$ according to reactions (12) or (13) relative during the lifetime of the excited state. Maximum length of the quantum chain which is in that case equal to the maximum quantum yield is significantly lower than for the reaction of photo-excited $\mathrm{Eu(fod)_3}$ with AAD where it was 118 [42]. This is probably caused by the low lifetime of $\mathrm{Pr(fod)}_3^*$. We could not measure the excitation lifetime of $\mathrm{Pr(fod)_3}$ for the low intensity of PL although it should not exceed $10^{-6}$ s [64,65], while this value for $\mathrm{Eu(fod)_3}$ is $2 \times 10^{-4}$ s ($t = 25°\mathrm{C}$, benzene) [20].

### *3.5. Quantum chain reactions in AAD–Pr(fod)$_3$ system*

The quantum chain decomposition of dioxetanes results in the increase of the observed rate of dioxetane consumption and in the lowering of the CL yield [35–40].

The evidence for QCR at photolysis in the $\mathrm{Pr(fod)_3}$–AAD system is a maximum quantum yield of the photo decomposition exceeding unit. Obviously, the QCR should also take place upon chemiexcitation of $\mathrm{Pr(fod)_3}$ in the $\mathrm{Pr(fod)_3}$–AAD system. Occurrence of the QCR in the $\mathrm{Pr(fod)_3}$–AAD system at chemiexcitation is indicated by an anomalous dependency of the observed decomposition rate of AAD and CL intensity on the $\mathrm{Pr(fod)_3}$ concentration (Figs. 1 and 2). Moreover, the high yield of $\mathrm{Pr(fod)_3}$ chemiexcitation favors the appearance of QCR. Taking into account that several electronic excited levels ($^3\mathrm{P}_1$, $^3\mathrm{P}_0$, $^1\mathrm{D}_2$) are populated at chemiexcitation of $\mathrm{Pr(fod)_3}$ and that the deactivation of $\mathrm{Pr}^{3+}*$ undergoes in subsequent processes $^3\mathrm{P}_1 \rightarrow ^3\mathrm{P}_0 \rightarrow ^1\mathrm{D}_2 \rightarrow$ [64,65], one may suppose that quenching of $\mathrm{Pr}^{3+*}$ by dioxetane or by the complex AAD·$\mathrm{Pr(fod)_3}$ may result in the decomposition of dioxetane with regeneration of $\mathrm{Pr}^{3+*}$.

Linear chains may be realized in the reaction of photo- or chemiexcited $\mathrm{Pr(fod)_3}$ in the $^3\mathrm{P}_1$ or $^3\mathrm{P}_0$ or $^1\mathrm{D}_2$ state with AAD accompanied by regeneration of $\mathrm{Pr(fod)}_3^*$:

$$\begin{aligned}&\mathrm{Pr(fod)}_3^*({}^3\mathrm{P}_1\ \mathrm{or}\ {}^3\mathrm{P}_0\ \mathrm{or}\ {}^1\mathrm{D}_2) + \mathrm{AAD} \rightleftarrows \mathrm{AAD} \cdot \mathrm{Pr(fod)}_3{}^* \\ &\quad \rightarrow \alpha \mathrm{Pr(fod)}_3{}^*({}^3\mathrm{P}_1 \ \vee {}^3\mathrm{P}_0\ \mathrm{or}\ {}^1\mathrm{D}_2) \\ &\quad + (1-\alpha)\mathrm{Pr(fod)}_3 + 2\mathrm{Ad{=}O}\end{aligned} \tag{18}$$

Quenching of one molecule of $\mathrm{Pr(fod)}_3^*$ by an AAD molecule Eq. (18) results in the regeneration of $\mathrm{Pr(fod)}_3^*$ with efficiency $\alpha$. The model of linear chain decomposition of AAD Eq. (18) easily explains the increase of $k_\mathrm{obs}$ with $\mathrm{Pr(fod)_3}$ concentration in the range $[\mathrm{Pr(fod)_3}] > 3.5 \times 10^{-2}$ M but it cannot explain the increase of CL intensity in the same range. Indeed the result of Eq. (18) should be either quenching or at least reaching of the limit value of CL intensity. For explanation of anomalous enhancement of CL intensity one should admit that with the increase of the $Pr(fod)_3$ or AAD·$Pr(fod)_3$ concentration, the increase of the concentration of $Pr(fod)_3^*$, i.e. the branching of the chain occurs. The branching of the chain may result from quenching of $Pr(fod)_3^*$ by AAD·$Pr(fod)_3$ with transfer of the energy quantum equal to the value of the energy gap of the $^3P_0 \rightarrow ^1D_2$ transition upon vibration overtones of dioxetane and preservation of excitation of $Pr^{3+}$ in the lower lying $^1D_2$ state. Energy transfer on AAD results in the decomposition of dioxetane and formation of $Pr^{3+}$ in the excited $^3P_1$ or $^3P_0$ or $^1D_2$ state due to the energy released in the reaction similar to Eq. (16):

$$\begin{aligned} &\mathrm{Pr(fod)_3}^*(^3\mathrm{P}_0) + \mathrm{AAD}\cdot\mathrm{Pr(fod)_3} \rightarrow \mathrm{Pr(fod)_3^*}(^1\mathrm{D}_2) \\ &\quad + \alpha\mathrm{Pr(fod)_3}^*(^3\mathrm{P}_1\,\mathrm{or}\,^3\mathrm{P}_0\,\mathrm{or}\,^1\mathrm{D}_2) \\ &\quad + (1-\alpha)\mathrm{Pr(fod)_3} + 2\,\mathrm{Ad}=\mathrm{O} \qquad (19) \end{aligned}$$

$Pr(fod)_3$ in the $^1D_2$ state formed upon quenching and the excited $Pr(fod)_3$ formed on decomposition of AAD·$Pr(fod)_3$ Eq. (19) may again react with AAD or AAD·$Pr(fod)_3$. The cascade dissipation of excitation energy upon vibration overtones of the surrounding molecules when excitation deactivates in subsequent transitions from one excited level to the lower one and not from the transition from the higher lying level directly to the ground level is used to explain the deactivation processes of the excited lanthanide ions [64,65]. The energy of the transition $^3P_0 \rightarrow ^1D_2$ in $Pr^{3+}$ is 3900 $cm^{-1}$ and it is close to the frequency of the fourth overtone of O–O bond in dioxetane ($\nu_0 = 886$ $cm^{-1}$) [53]. It should be noted that dioxetane decomposition may result from the transfer of the whole energy of the $^3P_0$ state of $Pr^{3+}$ as in Eq. (13).

Also, the growth of the number of excited $Pr^{3+}$ may occur upon quenching of the $Pr^{3+}$ in the $^3P_1$ excited state due to the transfer on the vibration overtones of AAD of the energy quantum of $^3P_1 \rightarrow ^3P_0$ (550 $cm^{-1}$) or $^3P_1 \rightarrow ^1D_2$ (4460 $cm^{-1}$) transition in the reaction similar to Eq. (19). Though the contribution of this route should be low enough since the $^3P_0$ and $^1D_2$ excited states of $Pr^{3+}$ are preferably formed on AAD·$Pr(fod)_3$ decomposition. Moreover, the lifetime of $^3P_1$ state should be lower than that for the $^3P_0$ and $^1D_2$ excited states.

Contribution of reaction (19) should be significant at the excess of chelate relative to dioxetane at the condition when almost all of the dioxetane is bound in complex AAD·$Pr(fod)_3$. Such conditions are realized upon kinetical experiments and we think that reaction (19) leads to the effective catalysis of AAD decomposition and anomalous enhancement of CL intensity at $[Pr(fod)_3]_0 > 3.5 \times 10^{-2}$ M Eqs. (1) and (2).

The quenching of $Pr(fod)_3^*$ in the $^3P_0$ state with preservation of excitation in the $^1D_2$ state by the complex AAD·$Pr(fod)_3$ Eq. (19) is proved by concentration dependence of CL intensity in different spectral regions (Fig. 8). CL intensity in the region 400–550 nm where CL is observed only from the $^3P_1$ and $^3P_0$ states reaches saturation while CL intensity in the spectral region 550–720 nm where the emission is partly due to the transitions from the $^1D_2$ level (the $^1D_2 \rightarrow ^3H_4$ and $^1D_2 \rightarrow ^3H_6$ transitions) repeats the behavior of the dependencies shown in Figs. 1 and 2. This should have been expected since according to Eq. (19) the quenching of the $^3P_0$ state occurs and as a result the $^1D_2$ state of $Pr^{3+}$ is formed. Similar quantum chain process with branching resulting from the quenching of excited $Eu(fod)_3^*$ by AAD·$Eu(fod)_3$ complex is observed in solution and on a sorbent surface in AAD–$Eu(fod)_3$ system.

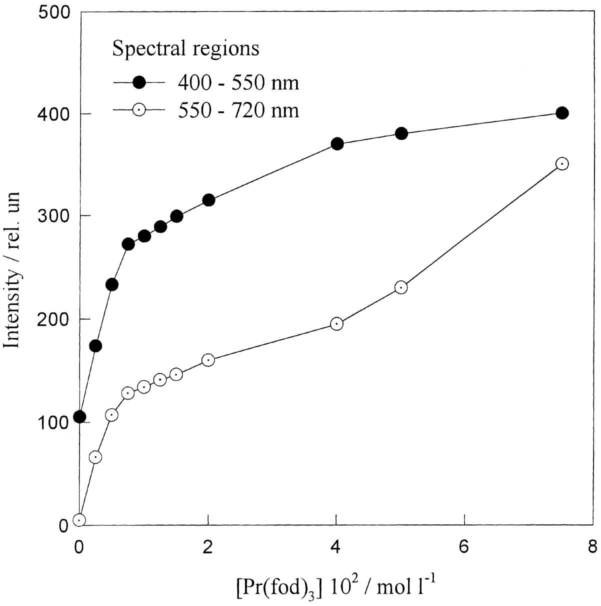


Fig. 8. Dependence of intensity of CL upon thermolysis of $10^{-3}$ M AAD at 75°C in toluene upon $Pr(fod)_3$ concentration in different spectral regions.

The conditions for the branched QCRs may be formulated as follows: (a) the population of several long-living electronic levels in rare earth ion; (b) regeneration of the excited state of rare earth ion upon chemical quenching of the excited state of RE ion by dioxetane; (c) quenching of the higher lying excited states of RE ion by dioxetane or by a [dioxetane·RE compound] complex with the partial reservation of excitation on the resonant level of RE ion.

## 4. Conclusions

The investigated CL system consisting of coordination unsaturated chelate $Pr^{3+}$–AAD is an example of a reaction when excitation of RE ion occurs through the highly exothermic reaction taking place in the inner coordination sphere of luminescent metal ion. This peculiarity leads to the observation of the differences observed in the emission spectrum of chemiexcited chelate (CL spectrum) compared with its spectrum of PL. We think that this phenomenon is general and it should be expected with other complexes of lanthanide ions. High efficiency of chemiexcitation of lanthanide chelates and lability of dioxetanes towards irradiation results in the QCR of dioxetane decomposition which can be considered as a model of chain electronic energy transfer with the participation of metal complexes.

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