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Chemiluminescence of Pr^{3+} in the visible region from the $^3P_1$, $^3P_0$, $^1D_2$ levels upon decomposition of adamantylideneadamantane-1,2-dioxetane catalysed by -diketonates $Pr(fod)_3$ and $Pr(dpm)_3$. An unusual route for activator chemiexcitation

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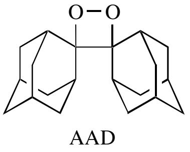
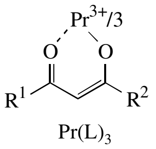
Chemiluminescence of Pr^{3+} is observed upon decomposition of adamantylideneadamantane-1,2-dioxetane (AAD) catalysed by -diketonates $Pr(L)_3$ (L = fod or dpm), the excitation of Pr^{3+} occurring through intracomplex energy transfer from the excited adamantanone formed upon decomposition of AAD in the complex $Pr(L)_3{\cdot}AAD$.

Dioxetanes are energy rich four-membered cyclic peroxides that readily decompose to give excited, mainly triplet, carbonyl products.[1] The decomposition is catalysed by metal complexes. The population of the electronically excited states (the chemiexcitation) of the complex may occur upon catalysis due to the energy released upon peroxide decomposition. The excited state of the catalyst then deactivates either nonradiatively or with the emission of chemiluminescence (CL).[2,3] In the latter case the chemiluminescence spectrum observed will not coincide with the photoluminescence (PL) spectrum of the same complex, since the chemiexcitation route differs from that of photoexcitation. So, effective chemiluminescence from the $^5D_1$ state of Eu^{3+} is observed,[4] amounting to 30% of the total Eu^{3+} CL intensity in the decomposition of adamantylideneadamantane-1,2-dioxetane (AAD) catalysed by -diketonate $Eu(fod)_3$. In contrast, the photoluminescence from the $^5D_1$ level of Eu^{3+} in solution[5] is less than 1% of the total emission intensity of Eu^{3+}.

We have observed that the CL intensity upon AAD decomposition in the presence of $Pr(fod)_3$ was comparable with that in the AAD–$Eu(fod)_3$ system, which is due exclusively to the chemiluminescence of Pr^{3+}, although the quantum yield of PL for $Eu(fod)_3$ ($\varphi_F = 5\%$) is much higher than that for $Pr(fod)_3$ ($\varphi_F \approx 0.1\%$). Taking into account this unusual result, and finding that no information concerning the photo- and chemiluminescence of the complexes of Pr^{3+} is available in the literature, we have studied the CL of Pr^{3+} arising in the decomposition of AAD in the presence of -diketonates $Pr(fod)_3$ and $Pr(dpm)_3$ and revealed the step leading to the chemiexcitation of Pr^{3+}.



AAD



$Pr(L)_3$

L = (fod): $R^1 = Bu^t$, $R^2 = C_3F_7$
L = (dpm): $R^1 = R^2 = Bu^t$

-Diketonates $Pr(L)_3$ were purified by sublimation and were dried before use at 70 °C under vacuum. All the experiments were carried out in toluene which was dried by boiling over metallic sodium then distilled. The synthesis and purification of other chemicals and the equipment used were described elsewhere.[3,4,6]

AAD in toluene solution decomposes to give two molecules of adamantanone (Ad=O), which may be formed in ground or excited singlet or triplet states (1). The CL upon AAD decomposition is due to the radiative deactivation of singlet adamantanone (λ_{max} = 420 nm, ϕ_{fl} = 0.015):[7]

$$\text{AAD} \longrightarrow 1.83\,\text{Ad=O} + 0.15\,\text{Ad=O}^*_T + 0.02\,\text{Ad=O}^*_S \qquad (1)$$

The AAD is one of the most stable dioxetanes, the activation parameters of its decomposition[7] being lg A = 14.1, E_a = 34 kcal mol^{-1}. Addition of $Pr(L)_3$ to a solution of AAD accelerates by more than 10^2 times the observed rate of decomposition. At the same time, the activation energy of the reaction is lowered, being 26±2 kcal mol^{-1} for $Pr(fod)_3$ as measured from the kinetics of the CL decay and 25±2 kcal mol^{-1} for $Pr(dpm)_3$ as measured from the temperature dependence of the quasi stationary CL intensity. The catalysis occurs through the formation of the complex $Pr(L)_3{\cdot}AAD$ where Pr^{3+} is coordinated by the oxygen atoms of the peroxide ring[1,4,6] (2):

$$\text{AAD} + \text{Pr(L)}_3 \rightleftharpoons \text{AAD}{\cdot}\text{Pr(L)}_3 \qquad (2)$$

The Pr^{3+} compounds are only weakly fluorescent in solution upon excitation into the ff absorption bands,[8] so the luminescence quantum yield for the chelates $Pr(L)_3$ at 20 ° is $\phi_{Pr} < 10^{-3}$. Nevertheless, the addition of $Pr(fod)_3$ (5×10^{-3}–7×10^{-2} M) to AAD (10^{-3} M) solution enhances the CL intensity by more than 10 times, and changes completely the CL spectra [Figure 1(*a*)]. The CL intensity upon addition of $Pr(dpm)_3$ (5×10^{-3}–3×10^{-2} M) to an AAD (10^{-3} M) solution increases only slightly, and is accompanied by quenching of CL in the region < 420 nm and CL enhancement in the region > 470 nm.

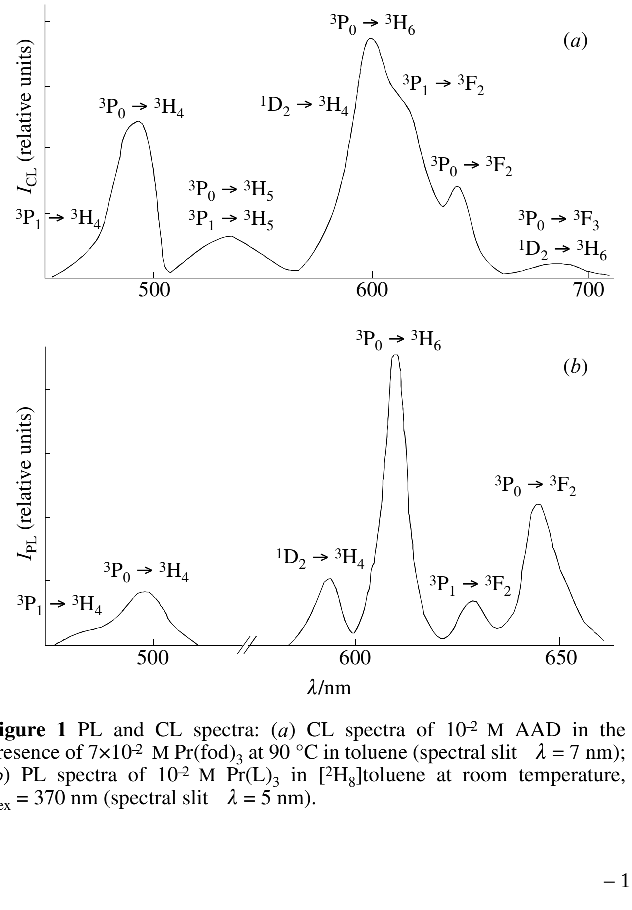


Figure 1 PL and CL spectra: (*a*) CL spectra of 10^{-2} M AAD in the presence of 7×10^{-2} M $Pr(fod)_3$ at 90 °C in toluene (spectral slit λ = 7 nm); (*b*) PL spectra of 10^{-2} M $Pr(L)_3$ in $[^2H_8]$toluene at room temperature, λ_{ex} = 370 nm (spectral slit λ = 5 nm).

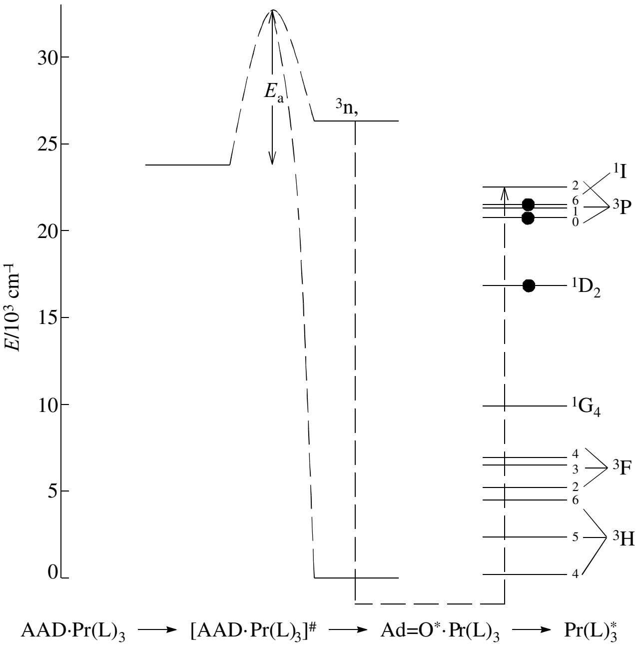


Figure 2 Energy scheme for AAD decomposition in the complex Pr(L)$_3$·AAD. The energy of the triplet adamantanone[11] $E_T = 75.2$ kcal mol^{-1}; the enthalpy of decomposition of 1,2-dioxetane[12] is $H \approx 68$ kcal mol^{-1}. Photo- and chemiluminescence are observed from the Pr^{3+} levels marked by (•).

AAD decomposition and chemiluminescence in the presence of Pr(L)$_3$ can be represented by various reactions, including decomposition of AAD in the complex AAD·Pr(L)$_3$ with excitation of Pr^{3+}, energy transfer from triplet adamantanone to Pr(L)$_3$ and light emission from excited chelate[1,4,6] (3)–(6):

$$\mathrm{AAD{\cdot}Pr(L)_3} \longrightarrow \phi_{\mathrm{Pr}^*}[\mathrm{Ad{=}O{\cdot}Pr(L)_3^* + Ad{=}O}] + (1-\phi_{\mathrm{Pr}^*})[\mathrm{Ad{=}O{\cdot}Pr(L)_3 + Ad{=}O}] \tag{3}$$

$$\mathrm{Ad{=}O{\cdot}Pr(L)_3^*} \longrightarrow \mathrm{Ad{=}O{\cdot}Pr(L)_3} + h\nu \tag{4}$$

$$\mathrm{Ad{=}O_T^* + Pr(L)_3} \longrightarrow \mathrm{Ad{=}O + Pr(L)_3^*} \tag{5}$$

$$\mathrm{Pr(L)_3^*} \longrightarrow \mathrm{Pr(L)_3} + h\nu \tag{6}$$

The step responsible for the chemiexcitation of Pr(L)$_3$ was revealed using adamantanone as a competitor with AAD in the complex formation reaction with chelate. When adamantanone (up to 10^{-1} M) is present in a solution containing chelate Pr(L)$_3$ (3×10^{-2} M) and AAD (10^{-3} M), the CL is quenched down to the level of CL emission in the absence of Pr(L)$_3$, with complete disappearance of the Pr^{3+} emission bands in the CL spectrum. Obviously the adamantanone decreases the concentration of Pr(L)$_3$·AAD by binding Pr(L)$_3$ in the complex Pr(L)$_3$·*n*Ad=O (*n* = 1 or 2) and thus quenching Pr^{3+} chemiluminescence. The main process leading to the excitation of Pr^{3+} is then an AAD decomposition reaction in the inner coordination sphere of Pr^{3+} in the complex Pr(L)$_3$·AAD followed by intracomplex energy transfer from excited adamantanone to Pr^{3+}.

The assignment of bands in the CL spectra was made from a comparison of the energy levels of the Pr^{3+} aqua ion[9] (Figure 2), and the absorption and PL [Figure 1(*b*)] spectra of Pr^{3+}.

Upon excitation of Pr(L)$_3$ in the ligand absorption band ($\lambda = 370$ nm) or in the ff absorption band of Pr^{3+} (^{3}H$_4$ → ^{3}P$_2$ transition, $\lambda = 450$ nm) extremely weak Pr^{3+} photoluminescence was observed with $\lambda_{\max} = 480$, 495, 595, 610, 625, 645 (±5) nm caused by radiative transitions from the ^{3}P$_1$, ^{3}P$_0$, ^{1}D$_2$ levels [Figure 1(*b*)].

The difficulties with band assignment in the PL spectrum of Pr^{3+} in the region 590–700 nm arises from bands overlapping, whereas the measurements at 400–550 nm were complicated by scattered light. The emission assigned to the ^{3}P$_1$ level may also originate from the ^{1}I$_6$ level, since the energy gap between ^{3}P$_1$ and ^{1}I$_6$ levels is only *ca.* 150 cm^{-1} and is comparable with the value of *kT* at room temperature.

The main part of the Pr^{3+} photoluminescence is observed not from the resonant ^{1}D$_2$ but from a higher lying ^{3}P$_0$ level, since for Pr^{3+} the disruption of cascading of non-radiative transitions in the system of ^{3}P$_1$, ^{3}P$_0$, ^{1}D$_2$ and ^{1}G$_4$ levels is observed,[10] which is caused by an anomalously low rate constant for non-radiative transition ^{3}P$_0$ → ^{1}D$_2$.

In the presence of adamantanone (up to 10^{-1} M) the intensity of PL for Pr(L)$_3$ (10^{-2} M) is enhanced by one order of magnitude, while AAD (2×10^{-2} M) only slightly enhances the PL of Pr(L)$_3$. In both cases no change in the shape of the PL spectra was observed.

Previously[2] the CL arising from catalysed decomposition of dioxetane derived from 9-(2-adamantylidene)-*N*-methylacridane by the complex Pr(fod)$_3$ was observed with a maximum in the CL spectrum at 602 nm ascribed to the emission of Pr^{3+}.

In the CL spectrum of the AAD–Pr(fod)$_3$ system many more maxima are observed at $\lambda_{\max} = 480$, 490, 535, 590, 605, 620, 640, 690 (±5) nm corresponding to the transitions originating from the ^{3}P$_1$, ^{3}P$_0$ and ^{1}D$_2$ levels of Pr^{3+} [Figure 1(*a*)]. The CL spectrum of the system AAD–Pr(dpm)$_3$ had a similar shape but such good resolution of the bands could not be achieved due to the low CL intensity.

As in PL the main part of the Pr^{3+} CL in the visible region originates from the ^{3}P$_0$ 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 [Figure 1(*a*)] 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 complexes [Pr(L)$_3$·*n*Ad=O]* (where *n* = 1 or 2) formed immediately after decomposition of dioxetane in the complex Pr(L)$_3$·AAD. It seems that the photophysical properties of such a chemically generated excited complex [Pr(L)$_3$·*n*Ad=O]*, namely the quantum yield and emission spectrum, differ from that of the chelate Pr(L)$_3$ or [Pr(L)$_3$·*n*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 and PL spectra.

An estimation of the excitation yield of Pr^{3+} ϕ_{Pr^*} upon AAD decomposition made from the absolute CL intensity, and kinetic measurements taking into account the fact that Pr^{3+} gets excited only in reaction (3) resulted in the value $\phi_{\mathrm{Pr}^*} < 10\%$.

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