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Quenching of the Triplet State of Benzophenone by Lanthanide 1,3-Diketonate Chelates in Solutions

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The phosphorescence of benzophenone in benzene and acetonitrile was quenched by several lanthanide (Sm, Eu, Gd, Tb and Dy) acetylacetonate chelates. The results of *Stern-Volmer* analysis including the quenching of benzophenone triplet and sensitization of lanthanide emission indicate that the quenching process occurs by the energy transfer mechanism via the excited triplet state of the ligand.

(Keywords: Acetylacetonate complexes of Sm(III), Eu(III), Gd(III), Tb(III) *and* Dy(III); *Energy transfer; Phosphorescence of benzophenone; Quenching; Sensitized fluorescence)*

Löschung des Triplettzustandes von Benzophenon mittels Lanthanid-1,3-Diketonat-Chelatverbindungen in Lösung

Die Phosphoreszenz von Benzophenon in Benzen und Acetonitril wurde durch 1,3-Diketonat-Chelatverbindungen von einigen Lanthaniden (Sm, Eu, Gd, Tb und Dy) gelöscht. Die Resultate der *Stern-Volmer*-Analyse einschließlich der Auslöschung des Benzophenon-Tripletts und die Sensibilisierung der Lanthanid-Emission zeigen, daß der Löschprozeß mittels Energieübertragungsmechanismus via angeregtem Triplettzustand des Liganden stattfindet.

Introduction

Quenching of the excited states of organic molecules by lanthanide ions in liquid solution has been the subject of numerous investigations, details of which may be found in a number of papers [1–4]. The two most prevalent quenching mechanisms have been shown to be the energy transfer and the electron transfer. The application of energy transfer process to spectroscopic determination of lanthanides is well known and often used as an analytical method [5]. It was found recently that acetylacetone used as a sensitizer lowered the limit of determination of *Ln*(III) ions in comparison with other methods known [6]. High sensitivity of the analytical method cannot be explained only by the physical energy transfer process, but probably also by the presence of complexes between acetylacetone and lanthanide ion. Therefore, it is important to put more light on the interaction of the excited states of organic molecules with the lanthanide 1,3-diketonate chelates. That type of interaction has been the subject of only a few studies [7–9]. The qualitative observation of the Eu(III) emission in europium hexafluoroacetylacetonate sensitized by aromatic carbonyls and aromatic hydrocarbons was explained by *El-Sayed* et al. [7] as a result of the efficient energy transfer process to the internal ligand triplet state from the triplet state of the organic sensitizer (donor):

$$T_{\text{donor}} \xrightarrow[\text{energy transfer}]{\text{intermolecular}} T_{\text{ligand}} \xrightarrow[\text{energy transfer}]{\text{intramolecular}} \longrightarrow \text{Eu(III)}^* \longrightarrow \text{emission} \qquad (1)$$

where * denotes the excited ff level of the Eu(III) ion ($^5D_0$). The involvement of ligand triplet state in the intramolecular energy transfer has been directly verified by *Matsuda* et al. [9].

To gain more quantitative information concerning the mechanism of the electronic energy transfer to lanthanide complexes we have examined the quenching of benzophenone phosphorescence by some lanthanide 1,3-diketonate chelates in solution at room temperature.

Materials and Methods

Benzophenone (reagent grade, POCh Gliwice) was recrystallized twice from ethanol. The trihydrate lanthanide acetylacetonates, $Ln(acac)_3 \cdot 3\,H_2O$, were prepared by standard techniques [10] and were recrystallized from ethanol. Elemental analyses were performed to check the purity of the samples and the results were in good agreement with the expected formulas (within 0.4%). $Eu(ClO_4)_3 \cdot 6\,H_2O$ and $Tb(ClO_4)_3 \cdot 6\,H_2O$ were prepared from Eu_2O_3 and Tb_4O_7 (spectral pure, prepared in our laboratory), respectively and recrystallized from ethanol. Benzene (for fluorescence, Merck) and acetonitrile (Uvasol, Merck) were used without further purification.

Absorption and emission spectra were taken with a Specord M-40 (Zeiss) spectrophotometer and a Perkin-Elmer MPF-3 spectrofluorometer, respectively. The emission spectra have been recorded in 1.0 cm cell using $\lambda = 375$ nm as an excitation wavelength.

The solutions with the constant concentration of benzophenone (0.0090 *M*) and concentrations of lanthanide chelates varying in the range of $10^{-6} - 10^{-4}$ *M* or perchlorates ($10^{-4} - 10^{-3}$ *M*) were used for emission analysis. In the experimental conditions used benzophenone was practically the only species absorbing the excitation light and hence the correction for the internal filter effect could be avoided. All samples were deoxygenated by bubbling oxygen free argon through the solution in the cell with the Rotaflo stopcock for 20 min.

Results and Discussion

Phosphorescence of benzophenone in liquid solution at room temperature is a well known phenomenon [11 a], and therefore, the quenching of benzophenone triplet state can be easily studied by the steady-state measurements using *Stern-Volmer* analysis [12]:

$$\frac{I_p^0}{I_p} = 1 + K[Q] \tag{2}$$

where

$$K = k_q \tau \tag{3}$$

and I_p^0 and I_p are phosphorescence intensities in the absence and presence of quencher, respectively, K is the *Stern-Volmer* quenching constant (M^{-1}), k_q is the quenching rate constant ($M^{-1}\,\mathrm{s}^{-1}$), τ is the lifetime of the benzophenone triplet in the absence of quencher (s), and $[Q]$ is the molar concentration of quencher (M).

If the energy transfer mechanism is the only quenching process the quantum yield of sensitized emission of the acceptor (Φ_Q) can be given by [13]:

$$\frac{1}{\Phi_Q} = \frac{1}{\eta_Q}\left(1 + \frac{1}{K[Q]}\right) \tag{4}$$

where η_Q is the efficiency of acceptor emission.

Dividing the intercept by the slope in Eq. (4), the *Stern-Volmer* quenching constant, K, can be obtained.

The quenching of benzophenone phosphorescence by lanthanide acetylacetonates such as Sm(*acac*)$_3$, Eu(*acac*)$_3$, Gd(*acac*)$_3$, Tb(*acac*)$_3$ and Dy(*acac*)$_3$ as well as sensitized emission of Eu(*acac*)$_3$ and Tb(*acac*)$_3$ were observed in benzene and acetonitrile at room temperature. The lack of sensitized emission of samarium and dysprosium acetylacetonates can be explained by the low values of their fluorescence quantum yield in comparison with Eu and Tb complexes [14]. In the case of Gd(*acac*)$_3$ which has its lowest radiative ff* level higher than the ligand localized triplet state an intramolecular energy transfer process [Eq. (1)] cannot take place and gadolinium emission is not observed.

In Fig. 1 the phosphorescence spectrum of benzophenone in the absence and presence of quencher Eu(*acac*)$_3$ is shown. The decrease of benzophenone phosphorescence and simultaneous increase in sensitized emission of Eu(III) with rising concentration of the quencher are observed. Typical *Stern-Volmer* plots for quenching and sensitized emission are presented in Figs. 2 and 3.

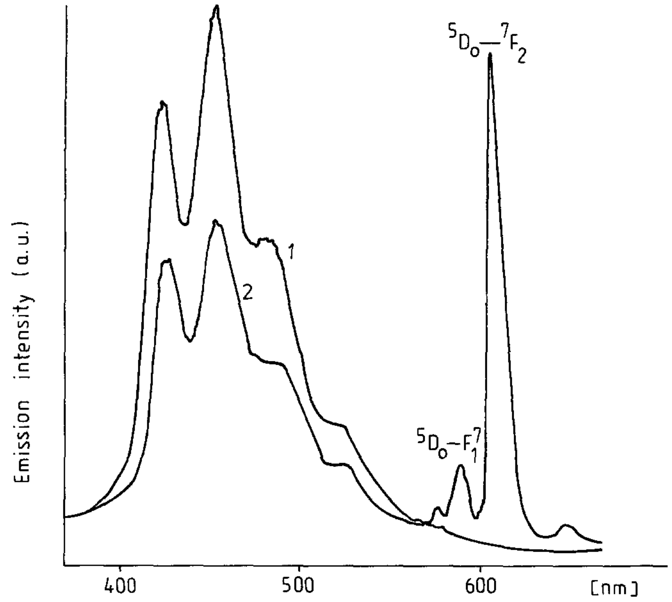

Fig. 1. Emission spectra of benzophenone in the absence (*1*) and in the presence (*2*) of Eu(*acac*)$_3$ in benzene solution at room temperature (uncorrected on apparatus response)

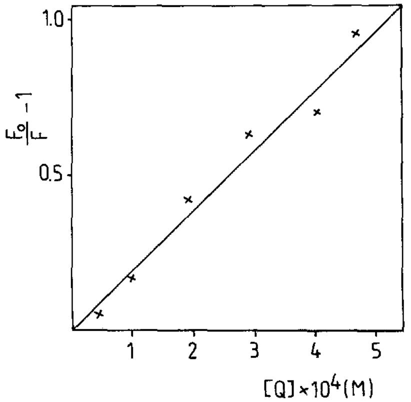

Fig. 2. *Stern-Volmer* plot [Eq. (2)] for quenching of benzophenone phosphorescence by Eu(*acac*)$_3$ in benzene ($\lambda_{ph} = 455$ nm)

It is important to note that the solutions of europium and terbium chelates do not reveal emission under the experimental condition used and a ground state complex between benzophenone and *Ln*(*acac*)$_3$ has not been detected in the absorption spectra. The presence of sensitized Eu(III)

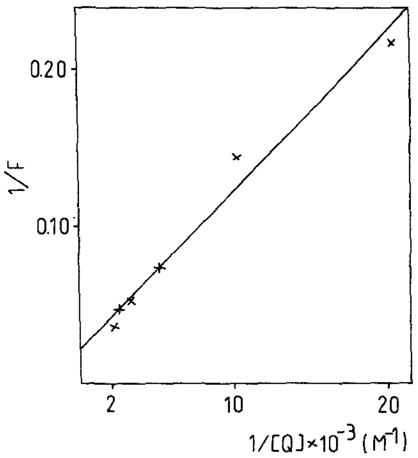

Fig. 3. *Stern-Volmer* plot [Eq. (4)] for emission of Eu(*acac*)$_3$ in benzene, sensitized by benzophenone (λ_{em} = 618 nm)

Table 1. *Quenching of benzophenone triplet state by lanthanide acetylacetonate chelates in benzene and acetonitrile at room temperature*

Compound	$K \cdot 10^{-3}$ (M^{-1}) from quenching of benzophenone phosphorescence, Eq. (2)		$K \cdot 10^{-3}$ (M^{-1}) from sensitized emission of *Ln*(III), Eq. (4)	
	Benzene	Acetonitrile	Benzene	Acetonitrile
Sm(*acac*)$_3$	1.75 ± 0.28	16.9 ± 1.5	—	—
Eu(*acac*)$_3$	1.93 ± 0.16	15.9 ± 1.2	2.3 ± 0.9	12 ± 3
Gd(*acac*)$_3$	1.55 ± 0.17	18.6 ± 1.5	—	—
Tb(*acac*)$_3$	1.70 ± 0.15	16.5 ± 1.6	~ 1.4	13 ± 5
Dy(*acac*)$_3$	1.90 ± 0.15	17.2 ± 1.7	—	—
Eu(ClO$_4$)$_3$	—	3.2 ± 0.3	—	[a]
Tb(ClO$_4$)$_3$	—	0.7 ± 0.2	—	[a]

[a] Lack of correlation with Eq. (4) (see [1])

and Tb(III) emission is direct proof of energy transfer involvement in the quenching process.

The quenching constants (*K*) obtained for *Ln*(*acac*)$_3$ are collected in Table 1. For the sake of comparison the quenching constants for terbium and europium perchlorates are also included.

Benzophenone phosphorescence is quenched by the lanthanide acetylacetonates with the same *Stern-Volmer* quenching constant for all

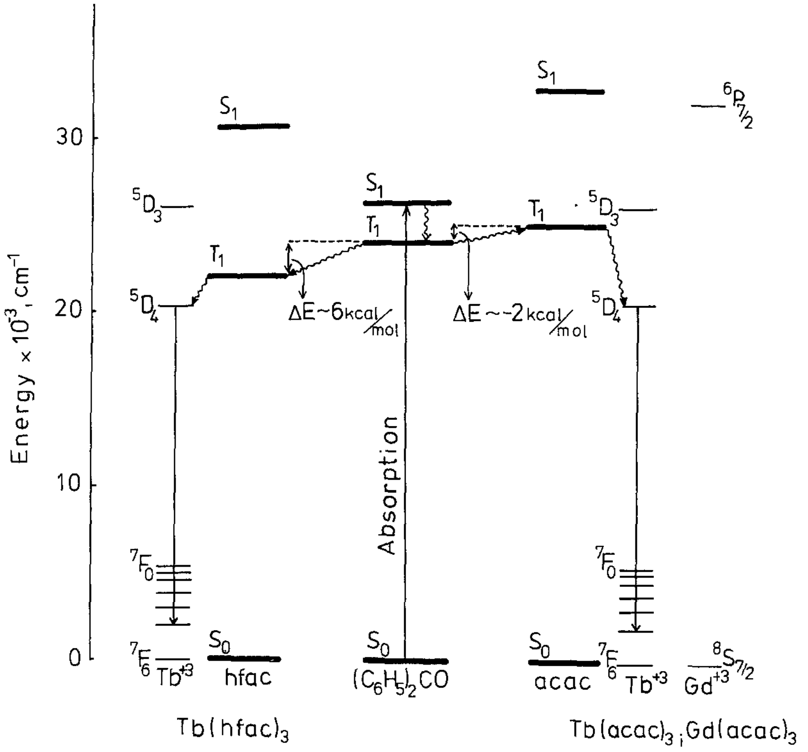

Fig. 4. Energy level diagram for the lowest excited states of benzophenone, Tb(*acac*)$_3$, Gd(*acac*)$_3$ and Tb(*hfac*)$_3$ (*hfac* hexafluoroacetylacetonate anion)

chelates used (~ $1.7 \cdot 10^3 M^{-1}$ in benzene and ~ $1.7 \cdot 10^4 M^{-1}$ in acetonitrile solutions). The lifetime of the benzophenone triplet state has been measured under identical experimental conditions using the quenching of benzophenone phosphorescence by Cu(*acac*)$_2$ as a standard [15]. On the basis of those results the quenching rate constant k_q ~ $6 \cdot 10^8 M^{-1} s^{-1}$ for *Ln*(*acac*)$_3$ in benzene and acetonitrile was calculated.

The values of K obtained in the quenching experiment with europium and terbium perchlorates have been at least five times lower than those of acetylacetonates. The appropriate k_q values have been calculated as ~ $1 \cdot 10^8 M^{-1} s^{-1}$ and ~ $2 \cdot 10^7 M^{-1} s^{-1}$ for Eu(III) and Tb(III) perchlorates, respectively, and are in agreement with the results reviewed in Ref. [1], where the formation of a complex between aromatic ketone triplet state and lanthanide ions has been suggested.

It is well known that the lanthanides are characterized by 4 f electrons which are shielded from their environment by an outer core of 5 s and 5 p electrons. Therefore, in general, the atomic properties of *Ln*(III) ions are almost always retained after formation of complex with organic ligands. Thus, the ligand excited levels and ff* levels of lanthanide ions can be treated separately as presented in Fig. 4.

The energy level diagram indicates that the physical energy transfer from the benzophenone triplet state to the lowest excited ff* level of Gd(*acac*)$_3$ is not possible. On the other hand similar values of the quenching constants obtained for all *Ln*(*acac*)$_3$ used, including also Gd(*acac*)$_3$, and comparable with those obtained from sensitized emission measurements indicate that the energy transfer takes place from the triplet state of benzophenone to the ligand localized excited triplet state.

That conclusion is additionally supported by the correlation of the quenching rate constant for *Ln*(*acac*)$_3$ with the energy gap between the excited states taking place in the energy transfer. It has been shown that the rate constants for triplet-triplet energy transfer in liquid solution is given by the equation [16]:

$$\frac{k_q}{k_d} = [1 + \exp - (E_T^D - E_T^Q)/RT]^{-1} \tag{5}$$

where $E_T^D - E_T^Q$ is the energy gap between the triplet states of donor (D) and acceptor (Q), k_d is the diffusion controlled energy transfer rate constant (equal to $1 \cdot 10^{10} M^{-1} s^{-1}$ in benzene, and $2 \cdot 10^{10} M^{-1} s^{-1}$ in acetonitrile at room temperature [11 b]).

Substitution of the values of triplet energies for benzene solutions at room temperature, i.e. $E_T^D = 24\,300\,\mathrm{cm}^{-1}$ [17] and $E_T^Q = 25\,000 \pm 200\,\mathrm{cm}^{-1}$ [18], into Eq. (5) gives $k_q/k_d \sim 3 \cdot 10^{-2}$ comparable with the estimated experimental value of k_q/k_d. Similar correlation can be obtained for acetonitrile solution. But taking into account the error of triplet state energy determination and the low value of the energy gap $(E_T^D - E_T^Q)$ (see Fig. 4), it was impossible to calculate an accurate value of k_q/k_d for acetylacetonate chelates. However, the same value of K for all *Ln*(*acac*)$_3$ and identical value of energy of the lowest excited triplet state of ligand (E_T^Q) for all *Ln*(*acac*)$_3$ [18, 19] indicate that the energy transfer process from the benzophenone triplet state to the ligand localized triplet state takes place.

On the other hand, the quenching of the benzophenone triplet state by hexafluoroacetylacetonates of europium and terbium was determined as a diffusion controlled process [7]. Taking into account Eq. (5) and the values of triplet state energy of benzophenone and hexafluoroacetylacetonate ligand ($E_T^Q = 22\,200\,\mathrm{cm}^{-1}$ [19]) the quenching process can be explained as a very efficient exothermic energy transfer from the triplet state of benzophenone to the ligand triplet state (Fig. 4).

The results obtained indicate that quenching of the benzophenone triplet state by the lanthanide 1,3-diketonate chelates occurs by an energy transfer mechanism via the excited ligand localized triplet state. This situation is quite different compared to the quenching of the excited aromatic ketone triplet states by the transition metal acetylacetonates, where both energy transfer (to d-d state) and electron transfer mechanisms are involved depending on the properties of the complex used [15, 17].

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