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The synthesis of (poly)hydroxycarboxylates
Part IV. Eu(III) promoted O-alkylation of glycolate with maleate as studied on-line by luminescence

Jeroen van Westrenen, Joop A. Peters*, Herman van Bekkum
Laboratory of Organic Chemistry, Delft University of Technology, Julianalaan 136, 2628 BL Delft (The Netherlands)

Jeannette Dexpert-Ghys* and **Bernard Piriou**
Laboratoire des Eléments de Transition dans les Solides, CNRS, 1 Place Aristide Briand, F-92195 Meudon Cédex (France)

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Abstract

The O-alkylation of glycolate with maleate yielding carboxymethoxysuccinate (cmos) is a lanthanide(III) promoted reaction. It is demonstrated that the reaction can be studied on-line with the help of an optical fiber setup, monitoring the luminescence of the Eu(III) optical probe. During the reaction the $^5D_0 \rightarrow {}^7F_0$ transition shifts to lower wavenumbers and the average lifetime of the excited $^5D_0$ level of the Eu(III) ion increases, when substantial amounts of Eu(cmos)$_2$ are formed. The average number of OH oscillators in the first coordination sphere of the Eu(III) ion is decreased by two if one cmos per Eu(III) is formed. The concentration of cmos can be obtained by on-line measurements of the lifetime of the $^5D_0$ excited state.

Introduction

Sequestering agents for lanthanide (Ln(III)) and alkaline earth metal ions are of special interest in the field of NMR imaging [1–3] and phosphate substitution in detergents [4–7]. Concerning the matter of phosphate substitution, oxygen containing polycarboxylates have been synthesized avoiding nitrogen in the chelate because of its potential threat to resolve heavy metal ion deposits in the environment. A possibility to synthesize these oxygen containing polycarboxylates is given by the Ln(III) promoted O-alkylation of hydroxycarboxylates and polyols with maleate [6, 8, 9]. The applicability of Ln(III) ions as a catalyst prompted us to study the Eu(III) promoted O-alkylation of glycolate with maleate (Scheme 1) by luminescence as a means of following the reaction on-line.

Scheme 1.

Luminescence studies on europium(III) complexes in aqueous solutions and solids have shown their versatility as an analytical tool [10]. The $^5D_0 \rightarrow {}^7F_0$ transition is non-degenerated by the crystal field Hamiltonian and, therefore, gives information on the number of crystallographic sites in a solid and on the minimum number of complexes present in solution [11–13]. The so-called 'nephelauxetic effect' is responsible for small shifts of the $^5D_0 \rightarrow {}^7F_0$ line position when Eu(III) is located in different environments [11]. Furthermore, the splitting of the $^5D_0 \rightarrow {}^7F_j$ ($j > 0$) manifold by the ligand field provides structural information on the Eu(III) complexes [14]. In addition, the lifetime of the $^5D_0$ excited state is used to determine the average number of waters (OH oscillators) in the first coordination sphere of the Eu(III) ion.

The on-line monitoring of the reaction was eased by using an optical fiber setup wherein one fiber conducted the excitation laser beam to the solution and six other fibers collected and guided the emitted light to the spectrometer. The use of optical fibers is one of the fastest growing areas in analytical and biomedical chemistry [15, 16]. The fluorescence of the medium can be monitored as such, or by specially attached physical or chemical sensors at the end of the optical fiber that emits light [17]. The method

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*Authors to whom correspondence should be addressed.

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is especially suited for analysis in inaccessible or hazardous environments. For instance, the analysis of the ground water [18] or the determination of the uranium(VI) content in a nuclear fuel reprocessing facility [19] have been described. The sensitivity of the analyses does not change upon extending the fiber length to one kilometer. The fact that one laser can handle several fiber devices makes the method of analysis extremely valuable for a remote on-line analysis in industrial processes.

Experimental

Materials

$EuCl_3 \cdot 6.5H_2O$ (99.9%) was purchased from Aldrich. The Eu(III) content was determined by ethylenediaminetetraacetate titration with xylenol orange as the indicator. Glycolic acid (Hga) was obtained from Merck-Schuchardt. The other chemicals were obtained from Aldrich. The trisodium salt of cmos was prepared as described previously [6]. The sodium salts of glycolate (Naga) and maleate (Na_2male) were made by neutralization of an aqueous solution of the acids by NaOH, followed by precipitation with an excess of ethanol.

O-alkylation of glycolate with male promoted by Eu(III)

The aqueous solutions of Na_2male, Naga and Eu(III) were heated in a reaction vessel at 363 K in a glycerol bath. The pH of the solution was recorded during the reaction at 363 K as described previously [9]. The samples from the reaction mixture were analyzed by HPLC [9].

The reaction in D_2O was performed with $EuCl_3 \cdot 4H_2O$, which was obtained after drying $EuCl_3 \cdot 6.5H_2O$ *in vacuo* at 353 K for 300 min. The reaction mixture was prepared by dissolving $EuCl_3 \cdot 4H_2O$ (1.648 g, 5 mmol), Na_2male (2.407 g, 12.52 mmol) and Naga (1.481 g, 12.76 mmol) in 25 ml D_2O.

Fluorescence measurements during the reaction

The experimental setup for *in situ* monitoring of the Eu(III) luminescence consists of three components: the reaction vessel, the spectroscopic part and the optical fiber device.

A specially designed reaction vessel was used in order to monitor the pH and luminescence simultaneously, by dipping both the pH electrode and optical fiber bundle into the solution. The tips of the fibers were just below the surface (<2 mm) and 4 cm above the bottom of the vessel if 15 ml of reaction mixture was used. Under these conditions the overlapping cone between the exciting light and the light collection cones was sufficient to ensure a high signal to noise ratio.

A pulsed nitrogen laser-pumped dye laser system (Jobin Yvon LAO4/E1T) was used for the selective excitation into the $^5D_2$ level of Eu(III). The maximum emission was observed for exciting at 4646 Å (21522 cm^{-1}) at 363 K and the dye laser was tuned to this wavelength for all the experiments. The $^5D_0 \rightarrow {}^7F_j$ emission was analyzed by a Coderg PHO double monochromator spectrometer equipped with a Hamamatsu 1477 photomultiplier. The $^5D_0 \rightarrow {}^7F_2$ emission was recorded at 6156 Å (16244 cm^{-1}) for measuring the lifetime (τ) of the $^5D_0$ level. For each excitation pulse the shape of the $^5D_0$ decay ($I = f(t)$) was extracted from a Tektronix 2430 digital oscilloscope by a hooked on BFM 187 16 bit computer. A program has been written in order to calculate the $^5D_0$ lifetime at equal intervals during the reaction. The numerical $I = f(t)$ values were averaged by the oscilloscope and transmitted at a frequency of about 0.5 Hz. Between two transmissions the computer calculated the lifetime τ by linear regression of the slope of log $I(t)$. The first 50 μs after the pulse were not taken into account so that the parasitic effects on the feeding of $^5D_0$ level from the upper $^5D_1$, $^5D_2$ levels as well as those of scattered incident light at very short delays do not affect the numerical values. The lifetime of the $^5D_0$ level was calculated for three time intervals after the pulse: Δt to $6\Delta t$, $6\Delta t$ to $12\Delta t$, and $12\Delta t$ to $16\Delta t$ using $\Delta t = 50$ μs in water at 363 K for lifetimes ranging from 200 to 500 μs. After a selected number of iterations (300) the three averaged values of τ were saved in an array and the process was repeated during the reaction time (up to 3 h). The τ values calculated for the three time intervals were in very good agreement ($\pm 3\%$) proving that the $^5D_0$ decays were single exponential. The time required for 300 iterations including the calculation of τ was 175 s. The average values of τ were assigned to the average time of each interval (175 s).

Emission lines originating from various ^5D_j levels or from $^5D_0$ of Eu(III) ions in different environments often exhibit differences in time evolutions. These differences are shown by different relative intensities of the emission recorded at short and long delays after the pulse. The same setup of the spectrometer was used as described above to record the time-resolved spectra. The computer numerically integrates the $I = f(t)$ function with selected gates and delays after the pulse. During one scan of the spectrometer, several time resolved spectra were recorded.

The third part of the experimental setup was an optical fiber device employed to guide the exciting laser light into the solution, collect the emitted light, and guide it back to the entrance slits of the spectrometer. Another experimental setup with an optical coupler between the incident and collection fibers had already been described by some of us [20], which was particularly useful for collecting spectroscopic information at low temperatures with small (all silica, 200 μm core) fibers. For the experiments described here, however, bigger fibers (Quartz et Silice plastic clad silica, 600 μm core) were perfectly suited using one fiber carrying the laser light to the sample and six collecting the light of the luminescence signal. The tips of the seven fibers were fixed in a compact hexagonal arrangement. The central fiber was used for the input light, while its other end was positioned in front of the dye laser, the laser beam was focused by a microscope objective (focal length 2 cm). The six fibers for collecting the signal were arranged in a line parallel to the slit of the spectrometer and the output was imaged by a collecting optical system on the entrance slit, this setup is analogous to that described by Schwab and McCreery [21]. A very good signal to noise ratio was achieved with this fiber device for the lifetime measurements (spectral resolution is 12 cm^{-1}) and an acceptable signal remained for most of the spectra recorded at 4 cm^{-1} spectral resolution.

Optical fibers proved to be more easier to install than conventional heated cells and allowed measurements on a relatively small volume of solution at 363 K. This could even be reduced to 1 ml if the pH was not monitored. The major experimental problem appeared to be the evolution of gas bubbles in the heated solution, even after degassing, that set on the fiber tips and decreased the signal collected. These phenomena hampered the determination of the kinetics via monitoring the peak intensities at a particular wavelength. This artefact, however, did not affect the lifetime values.

Results and discussion

Reaction characteristics

The O-alkylation of ga with male yielding carboxymethoxysuccinate (cmos) promoted by Ln(III) ions occurs in a relatively concentrated reaction medium (0.2 M Eu(III)) at 363 K and at a pH that is high enough to ensure the ionization of the hydroxyl group of a coordinated ga ligand in the ternary complex Eu(male)(ga)$_n$ ($n = 1$, 2). A pK_a of 7.8 of the hydroxyl group of a Eu(III) coordinated ga ligand has been determined for the ternary complex Eu(male)(ga)$_n$ ($n = 1$, 2) at 363 K [9]. The formation of Ln(cmos)$_2$ complexes captures the Ln(III) ion from being involved in the reaction and, therefore, inhibits the reaction. The Ln(cmos) complex is still able to serve as a catalyst for the formation of a second molecule of cmos, but with a lower reaction rate constant than that of the Ln(III) ion (about six times for La(III) [6]).

TABLE 1. Association constants[a]

Species	Log β[b]
Eu(ga)	2.44
Eu(ga)$_2$	4.80
Eu(male)	2.99
Eu(male)$_2$	4.68
Eu(ga)(male)	5.09
Eu(cmos)	5.85
Eu(cmos)$_2$	9.98
Eu(cmos)(ga)	7.7[c]
Eu(cmos)(male)	7.6[c]

[a] $I = 1.0$ (NaClO$_4$), 298 K; ga: p$K_a = 3.62$; male: p$K_{a1} = 1.63$, p$K_{a2} = 5.62$; cmos: p$K_{a1} = 2.46$, p$K_{a2} = 3.60$, p$K_{a3} = 4.64$ from ref. 9. [b] $\beta = [Eu(L)(Z)]/([Eu(III)][L][Z])$. [c] Estimated statistically from both Eu(cmos)$_2$ and Eu(ga)$_2$ or Eu(male)$_2$ according to refs. 9 and 23.

Binary and ternary complexes of male and ga with lanthanide(III) ions are formed in the mixed ligand system. The complexes are in fast exchange with each other. Their stability constants have been measured by potentiometry at 298 K ($I = 1.0$ M, NaClO$_4$) (Table 1) [9]. NMR [22] and potentiometric studies [9] have shown that the product, cmos, can form 1:1 and 1:2 complexes with Ln(III) ions. As Eu(cmos)(L) (L = ga, male) complexes can be formed during the reaction, their stability constants were estimated statistically at 298 K according to Martin *et al.* [23] (see Table 1). These estimated stability constants were shown to be a good approximation of the experimentally determined ones for the Ln(male)(ga) ternary complex [9].

The reaction at 363 K is sufficiently slow to allow recording of changes of the speciation in the reaction mixture during the Eu(III) promoted O-alkylation with the use of the lifetimes of the $^5D_0$ level as a function of the reaction time. This lifetime was monitored at 16244 cm^{-1} at the maximum of the emission from $^5D_0$ ($^5D_0 \rightarrow {}^7F_2$ transition). To help in the interpretation of the average Eu(III) $^5D_0$ lifetime, complementary information was extracted from the comparison of the $^5D \rightarrow {}^7F_0$ emission shape in various Eu–cmos and Eu– male or Eu–ga solutions with the final reaction products.

$^5D_0 \rightarrow {}^7F_0$ emission spectra

In Fig. 1(a) and (b) the $^5D_0 \rightarrow {}^7F_0$ transition is shown for two ratios of Eu(III)/cmos (ρ_{cmos}) at 363 K. At Eu(III)/cmos ratios in between, it was shown

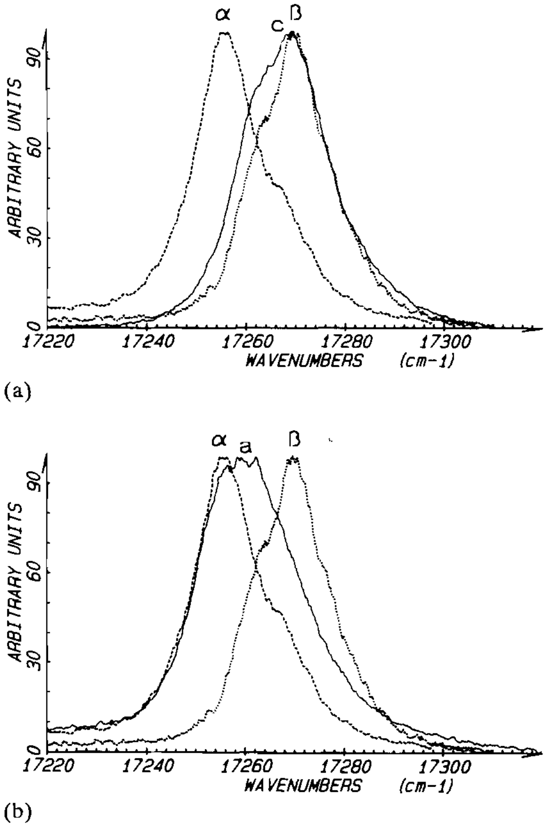

Fig. 1. $^5D_0 \rightarrow {}^7F_0$ emission at 363 K for the molar ratio Eu(III)/cmos = 0.5 (spectrum α, Eu(III) = 0.2 M, pH 6.15) and Eu(III)/cmos = 1.4 (spectrum β, Eu(III) = 0.1 M, pH 5.26). (a) Spectrum c is the $^5D_0 \rightarrow {}^7F_0$ emission at 363 K for the reaction mixture formed after 3 h at 363 K using a ratio Eu/male/ga = 1/1.3/1.3. (b) Spectrum a, as spectrum c using a ratio Eu/male/ga = 1/2.7/2.7. The labelling of the curves (a, c) corresponds to the experiments described in Table 3. Excitation 21522 cm^{-1}.

that the $^5D_0 \rightarrow {}^7F_0$ transition for both complexes are well separated. From these spectra it can be concluded that the wavenumbers of the Eu(cmos)^0 and Eu(cmos)$_2{}^{3-}$ complexes are 17270 and 17256 cm^{-1}, respectively. This is in agreement with the generally observed shifting to lower wavenumbers for higher charged complexes [11]. The shoulder in the spectrum measured at $\rho_{cmos} = 0.5$ might be assigned to the Eu(cmos) complex that is still present under these conditions. No change in the spectrum was observed upon cooling to 298 K. Only a slight displacement (3 cm^{-1}) towards lower energies was observed for both peaks. Changing the pH at this temperature from 6.55 to 4.5 does not affect the position of the peaks.

At 298 K the $^5D_0 \rightarrow {}^7F_0$ emission for the Eu(III)–male–ga mixed system can be studied because no reaction takes place at this temperature. A single peak was observed at 17264 cm^{-1} at a molar ratio of Eu(III)/male/ga of 1/2/2 (Eu(III) = 0.2 M), which is at the same wavelength as that of the Eu(cmos) complex at 298 K, although a large linewidth is observed in the case of the mixed ligand system.

In Fig. 1(a) the $^5D_0 \rightarrow {}^7F_0$ emission of the final reaction product of a reaction started with a Eu(III)/male/ga ratio of 1/1.4/1.4 (Eu(III) = 0.2 M) resulting in $\rho_{cmos} = 0.92$ (81% conversion) after 3 h is shown. This spectrum exhibits the $^5D_0 \rightarrow {}^7F_0$ signals of the Eu(cmos) complex and starting complexes, but the signal is much broader and displaced slightly to lower wavenumbers. This suggests that other complexes are formed, like ternary complexes of Eu(cmos)(L) (L = male, ga), or polynuclear complexes, which have $^5D_0 \rightarrow {}^7F_0$ transitions that are slightly shifted with respect to the transitions of the initial reaction mixture and Eu(cmos). In Fig. 1(b) the emission of the final reaction product is shown of a reaction with a ratio of Eu(III)/male/ga 1/2.7/2.7 (Eu(III) = 0.2 M). A $\rho_{cmos} = 0.72$ (51% conversion) is reached after 3 h. The broad peak a shows by its position that a considerable amount of Eu(cmos)$_2$ complex is present in this reaction mixture.

An estimation of the speciation at 298 K can be obtained using the association constants of Table 1 [24]. For the reaction mixture of Fig. 1(a) a distribution of Eu(cmos) (0.069 M), Eu(cmos)$_2$ (0.047 M), Eu(cmos)(male) (0.02 M), Eu(cmos)(ga) (0.03 M) can be calculated assuming that the concentrations of other complexes are negligible. Analogously, the speciation in the reaction mixture of Fig. 1(b) can be estimated: Eu(cmos) (0.003 M), Eu(cmos)$_2$ (0.094 M), Eu(cmos)(male) (0.04 M) and Eu(cmos)(ga) (0.045 M). The signal intensity at 17256 cm^{-1} of the $^5D_0 \rightarrow {}^7F_0$ spectrum of the reaction mixture in Fig. 1(a) seems to be too low for the calculated concentration of the Eu(cmos)$_2$ complex. This may be attributed to the relative intensity of the $^5D_0 \rightarrow {}^7F_0$ emission versus $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$, which is low for Eu(cmos)$_2$ compared to Eu(cmos), or to the assumptions in the model used (e.g. the neglect of polynuclear complexes [25]).

These experiments demonstrate that large effects on the wavenumber of the $^5D_0 \rightarrow {}^7F_0$ transition are only observed when the ligand concentration is high enough to ensure the formation of high concentration of Eu(cmos)$_2$. The information of the $^5D_0 \rightarrow {}^7F_0$ transition is somewhat limited due to the considerable overlapping of the emission lines because of their relative broadness and of the small difference in wavenumbers between the complexes formed (at most 15 cm^{-1} between the Eu(cmos) and Eu(cmos)$_2$ emissions).

On-line study of the reaction by the lifetime of the $^5D_0$ excited state

Lifetime of the $^5D_0$ excited state

Single exponential decay curves of the $^5D_0$ excited state were observed at 298 and 363 K, showing that the various species present in solution are in fast exchange with respect to the lifetime of the $^5D_0$ excited state. The average decay can be expressed as $n_t^* = n_0^* \exp(-Pav\ t)$, where n^* is the number of Eu(III) ions in the excited state and Pav is the average decay probability which is the inverse of the average lifetime (τ). In the fast exchange region n^* is defined by $K_i = n_i^*/n^* = n_i/n$ (n is the number of Eu(III) ions at the ground state level). $Pav = \Sigma K_i P_i$ with K_i being the relative concentration of species i per total concentration of Eu(III) present in the equilibrium [26]. The main pathway for non-radiative depopulation of the $^5D_0$ level of Eu(III) in aqueous solutions is by coupling with the high-energy OH vibrations, which will be discussed below.

Effect of the molar ratio of Eu(III)/ligand(s)

The lifetimes τ ($1/P$) of the $^5D_0$ excited state for mixtures with various molar ratios Eu(III)/ligand (ρ_{ligand}) are given in Table 2. The lifetime measured for $\rho_{\text{cmos}} = 0.5$ is the weighted averaged of a mixture of Eu(cmos) and Eu(cmos)$_2$. Comparison of the values obtained at 298 and 363 K shows that the lifetime is hardly dependent on the temperature. At $\rho_{\text{cmos}} = 0.2$ the lifetime is 500 μs at 298 K. This value was used as an estimate of the lifetime of the Eu(cmos)$_2$ complex at 298 and 363 K. The lifetime of the Eu(cmos) complex is calculated from the lifetime at $\rho_{\text{cmos}} = 1.4$ using the stability constants in Table 1, to be around 180 μs. At $\rho_{\text{male}} = 0.5$ a large increase of the $^5D_0$ lifetime (56 μs) is observed when raising the temperature to 363 K, which is in contrast to the generally observed decrease in lifetime at elevated temperatures [27]. A possible explanation is given by thermodynamic data, which show that the concentration of Eu(male)$_n$ ($n = 1, 2$) increases at higher temperatures [28]. Unfortunately, the lifetime of the complexes at a ratio of Eu(III)/ga of 1/2 could not be measured due to their low solubility.

TABLE 2. The lifetime of the $^5D_0$ excited state for various Eu(III)–ligand solutions: excitation 21522 cm^{-1}; observation 16244 cm^{-1}

Ligand(L)	Eu(III)/L (ρ)[a]	T(K)	pH[b]	τ (μs)
none		298	≈4	105
male	0.5	298	6.30	192
male	0.5	363	5.77	248
cmos	1.4	298	5.26	170
cmos	0.5	298	4.5	411
cmos	0.5	298	6.55	423
cmos	0.5	363	6.15	433
cmos	0.2	298	7.9	500
male, ga	0.5, 0.5	298	5.76	228
male, ga	0.5. 0.5	363	5.67	239[c]
male, ga, cmos	1, 1, 1	363	6.03	296

[a] 0.2 M Eu(III). [b] pH measured at the temperature indicated. [c] Obtained by extrapolation of reaction g in Fig. 5.

The data of Table 2 show that there is a general trend towards longer lifetimes upon increasing ligation of Eu(III) with organic ligands. This is accompanied by a shift to lower wavelength of the $^5D_0 \rightarrow {}^7F_0$ transition (see Fig. 1). These phenomena can be explained by the decrease of the number of Eu(III) coordinated water ligands upon an increase of the number of Eu(III) coordinated organic ligands, which lowers the efficiency of the quenching of the $^5D_0$ excited state, whereas the increased negative charge in the first coordination sphere of the Eu(III) ion lowers the wavelength of the $^5D_0 \rightarrow {}^7F_0$ transition [11].

As a consequence, the O-alkylation reaction with maleate can be monitored optimal by luminescence at a low molar ratio Eu/ligand, because in that case the increase of the lifetime of the $^5D_0$ excited state during the course of the reaction is relatively large. This is demonstrated in Fig. 2. At a high Eu(III)/(ga and male) ratio a small increase in lifetime is observed although the conversion to cmos is 81% after 3 h (Fig. 2, c). When a lower Eu(III)/(ga and male) ratio was used, a larger increase in lifetime is observed (Fig. 2, a). This is probably due to the formation of higher concentrations of Eu(cmos)(L) (L = ga, male or cmos), which is in agreement with the higher lifetime of the $^5D_0$ excited state compared

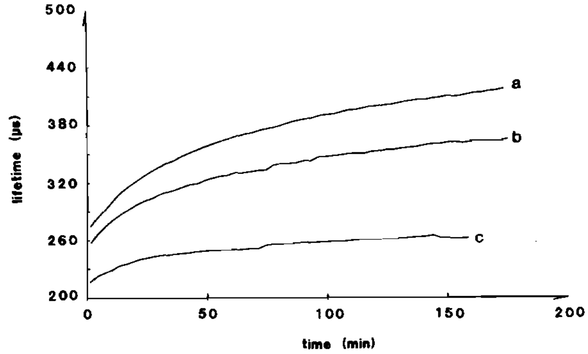

Fig. 2. On-line measurements of the $^5D_0$ lifetime during the reaction at various molar ratios Eu(III)/ligand at 363 K. The labelling of the curves corresponds to the experiments described in Table 3. Excitation 21522 cm^{-1}. Observation 16244 cm^{-1}.

to the lifetimes of the starting compounds and Eu(cmos) (Table 2).

Previously, we have studied the kinetics of the O-alkylation reaction by means of HPLC, using an excess of ga with respect to Eu(III) and male. Under these conditions there is also a big effect on the lifetime of the $^5D_0$ excited state (Fig. 3), demonstrating that this technique is very suitable for monitoring this reaction on-line. The lifetimes of the initial reaction mixtures were much higher than in experiments performed with a lower amount of ga.

Addition of extra ga to diluted samples of the starting solution (0.1 M Eu(III), reaction a) and final reaction mixtures showed increased lifetimes of 320 and 515 μs, respectively, at pH 6.7 and 363 K. This suggests that a shift in complex equilibria occurs to species with a higher number of coordinated ligands under these conditions.

The effect of the formation of cmos on the lifetime in both experiments is similar to that observed at a ratio of Eu/male/ga 1/2/2, which shows that the reaction can be monitored via the lifetime of the $^5D_0$ excited state at a large range of molar ratios male/ga.

Effect of pH on the lifetime of the $^5D_0$ excited state

Eu(III) coordinated di-ionized ga is a key intermediate in the O-alkylation reaction; and as a result the reaction rate is strongly dependent upon the pH of the reaction medium. Therefore, we have also investigated the influence of pH on the lifetime for the initial and final reaction mixtures in the pH range where O-alkylation takes place. Since no reaction occurs at 298 K, at this temperature the influence of the pH was studied with the initial reaction mixture (Eu(III)/male/ga = 1/2/2) and with a reaction mixture wherein 68% of cmos was present (reaction b, Table 3). Figure 4 shows that for both reaction mixtures the $^5D_0$ lifetime increases gradually (10 μs per pH unit) up to pH 6.8 and 7.5, respectively, and then steeply increases (100 μs per pH unit).

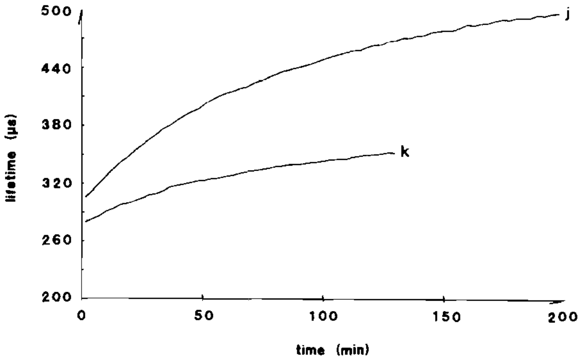

Fig. 3. On-line measurements of the $^5D_0$ lifetime during the reaction using an excess of ga: 0.10 M Eu(III), 0.20 M male and 1.0 M ga. Two reactions are monitored at 363 K having a difference in pH. The labelling of the curves corresponds to the experiments described in Table 3. Excitation 21522 cm^{-1}. Observation 16244 cm^{-1}.

The point at which the steep increase of the lifetime starts off corresponds with the pK_as of coordinated H_2O and the coordinated hydroxyl group of ga* and is probably caused by a decrease of the amount of OH oscillators in the first coordination sphere [29]. This may be explained by the displacement of bound waters by the di-ionized glycolate (H_{-1}ga) or by hydroxide ligands and by the formation of binuclear complexes. The sensitivity of the $^5D_0$ excited state to the formation of OH^- and H_{-1}ga ligands can be used to determine the optimal pH for a particular reaction mixture employed in the O-alkylation reaction.

The $^5D_0 \rightarrow {}^7F_0$ transition shows a small increase in linewidth (17→22 cm^{-1}) going from low to high pH. For the reaction mixture, containing cmos, two broad peaks were observed at pH 8.8 having different lifetimes. This points to two different complexes that might be formed by disproportion of the Eu(III) complexes to Eu(cmos)$_2$, and oligonuclear Eu(H_{-1}ga)$_n$ or Eu(OH)$_n$ complexes. An analogous phenomenon was observed for the La(nitrilotriacetate) complex at high pH with the use of ^{139}La NMR [9].

On-line study of the reaction by the $^5D_0$ lifetime: effect of pH

In the previous paragraph it is shown that the effect of pH on the lifetime during the reaction is small when the O-alkylations are performed below the pH of the transition point of the initial reaction mixture (pH 6.7, 298 K) (Fig. 4). This transition point can vary with temperature. When the O-alkylations were performed below pH 6.10 (363 K), only small variations of the lifetime as a function of the pH of the initial reaction mixture (30 μs per pH unit) were observed. Therefore, the increase in lifetime of the $^5D_0$ excited state of the Eu(III) ion upon progress of the reaction is mainly due to the increased amount of cmos in the speciation (Fig. 5). This, probably, also holds for the previously described experiments performed at various molar ratios Eu/ligands.

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*The pK_a for the ionization of a coordinated ga ligand in the Eu(male)(ga)$_n$ ternary complexes is calculated to be 7.8 (363 K) and the pK_a of a coordinated water is 8.3 (I = 0.3, 298 K).

TABLE 3. Reaction conditions, amount of cmos formed and calculated amount of OH oscillators for the reaction mixtures formed

Mixture	Initial reaction mixtures (M) [Eu], [male], [ga]	pH range[b]	cmos conc. (M)[c]	P_i (ms^{-1})[d]	P_f (ms^{-1})[d]	ΔOH[e]
a	0.200, 0.534, 0.547	6.24–6.09	0.276	3.69	2.39	2.9
b	0.200, 0.400, 0.410	6.01–5.97	0.272	3.97	2.73	2.7
c	0.200, 0.267, 0.267	5.31–5.01	0.216	4.72	3.80	2.1
d	[a]	6.15	0.397	2.30	2.42	0.3
e	0.200, 0.400, 0.410	6.07–6.17	0.282	3.97	2.70	2.8
f	0.200, 0.400, 0.410	5.85–5.72	0.258	4.10	2.94	2.6
g	0.200, 0.400, 0.410	5.67–5.43	0.238	4.18	3.05	2.5
h	0.200, 0.400, 0.410	6.15–6.04[f]	0.198	4.12	3.20	2.1
i	0.200, 0.400, 0.410	5.69–5.62[f]	0.134	4.27	3.72	1.2
j	0.100, 0.200, 1.00	6.97–7.64	0.160	3.32	2.02	2.9
k	0.100, 0.200, 1.00	6.29–6.00	0.076	3.61	2.84	1.7
l[g]	0.200, 0.500, 0.510	6.58–7.14	0.281	0.67	0.50	

[a] [Eu], [cmos] = 0.2, 0.398 M. [b] pH of the initial and final reaction mixture as measured at the reaction temperature (363 K). [c] Concentration of cmos formed in final reaction mixture as determined by HPLC. [d] Decay probability for initial (P_i) and final reaction mixture (P_f). [e] Variation of the concentration of OH oscillators in the first coordination sphere per Eu(III) in initial and in final reaction mixture as calculated by eqn. (3) with $(P_{OH} - P_{COO}) = 0.45\ ms^{-1}$. [f] Reaction at 343 K. [g] Reaction in D_2O at 363 K.

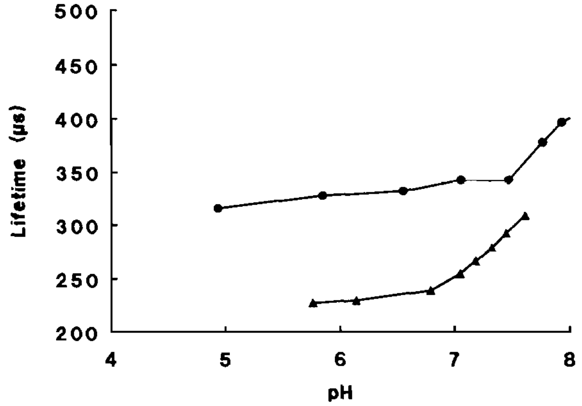

Fig. 4. Dependence of the lifetime of the $^5D_0$ excited state on the pH of an initial and a final reaction mixture at 298 K. Initial reaction mixture (▲): 0.20 M Eu(III), 0.41 M ga and 0.40 M male. Final reaction mixture (●): 0.20 M Eu(III), 0.138 M ga, 0.128 M male and 0.272 M cmos, obtained by heating the initial reaction mixture for 3 h at 363 K.

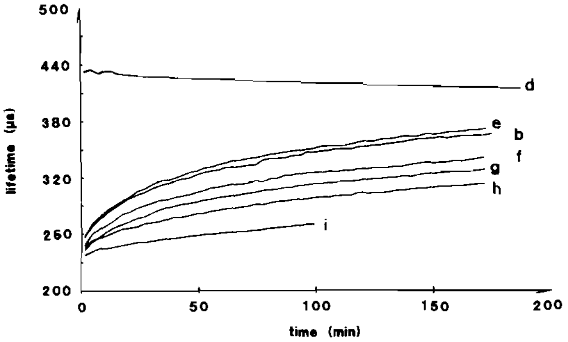

Fig. 5. On-line measurements of the $^5D_0$ lifetime during the reaction at slightly different pH values in the pH range from 6.1 to 5.7. A reaction mixture with a ratio Eu/male/ga of 1/2/2 was heated at 363 K (b, e, f, g) or at 343 K (h, i). Evolution of the lifetime as a function of time of a Eu/cmos mixture at 363 K (d). The labelling of the curves corresponds to the experiments described in Table 3. Excitation 21522 cm^{-1}. Observation 16244 cm^{-1}.

Amount of Eu(III) coordinated waters as measure for the amount of cmos formed

As shown in previous paragraphs, the on-line monitoring of the reaction is possible by the measurement of the $^5D_0$ excited state lifetime. In order to check if the measured parameter τ is actually related to the progress of the reaction, and because of the differences observed in the initial τ values of the different experiments (see Table 3), we compared the total lifetime increase $(\tau_f - \tau_i)$ in each experiment with the total amount of cmos formed as measured by HPLC.

The difference $(\tau_f - \tau_i)$ may be interpreted, in first approximation, as the expression of the variation in the average number of OH oscillators in the first coordination sphere of Eu(III). The observed decay probability P per species in aqueous solution is commonly described by the sum of a purely radiative part P_{rad} and a non-radiative part. The latter can be separated into coupling with OH vibrators, P_{OH}, and coupling with all other non-radiative pathways P_{nr} [30, 31]. Upon coordination of the aqua ion of

Eu(III) by the ligands used in this study, a number of Eu..H_2O bonds in the first coordination sphere are replaced by Eu..COO^- bonds. So, *Pav* of the $^5D_0$ excited state may be expressed by

$$P_{av}=\Sigma K_i(P_{rad}+P_{nr}+n_{OH}P_{OH}+n_{COO}P_{COO})_i \qquad (1)$$

When P_{av} is altered e.g. by the formation of cmos, the change of the decay probability can be expressed by eqn. (2), neglecting $\Delta(\Sigma K_i n_{COO,i})P_{COO}$.

$$\Delta P_{av}=\Sigma K_i(\Delta P_{rad}+\Delta P_{nr})_i+\Delta OH(P_{OH}-P_{COO}) \qquad (2)$$

In this equation $\Delta OH=\Delta(\Sigma K_i n_{OH,i})=-\Delta(\Sigma k_i n_{COO,i})$ is the variation of the average number of OH oscillators per Eu(III). If it is assumed that the variations in lifetime observed during the reaction are only dependent on the change of OH oscillators one neglects $(\Delta P_{rad}+\Delta P_{nr})$ e.g. other factors contributing to the decay of the $^5D_0$ excited state. Using this simplification one can write eqn. (3) for the difference of the decay probability between the starting and final composition

$$P_{av,initial}-P_{av,final}=\Delta OH(P_{OH}-P_{COO}) \qquad (3)$$

An estimation of $(P_{OH}-P_{COO})$ may be obtained from the decay probability for the $Eu(H_2O)_9$ species, and the Eu doped $\{Gd_2(H_2O)_6(oxalate)_3\}\cdot 4H_2O$ complex in which each Eu(III) is coordinated to three H_2O and six carboxylate groups [31]. A $(P_{OH}-P_{COO})$ value of 0.45 ms^{-1} per OH vibrator is obtained. About the same value is found using the lifetimes of the $Eu(H_2O)_9$, $Eu(cmos)\cdot 5H_2O$ and $Eu(cmos)_2\cdot 1H_2O$ complexes in solution at 298 K (see above). From the τ values of 105, 180 and 500 μs, respectively, a $(P_{OH}-P_{COO})=0.44\pm 0.3$ ms^{-1} can be calculated. A decay probability of the $^5D_0$ by coupling with an OH vibrator is estimated to be 0.5 ms^{-1} by measuring the lifetimes of the $^5D_0$ excited state as function of the amount of water in acetonitrile [32]. These values are in reasonable agreement with each other and show that coupling with the carboxylate group is a very inefficient non-radiative pathway. For the numerical estimation of the variation in coordinated water during the reaction (ΔOH), the average value of 0.45 ms^{-1} was used at 363 K, thereby neglecting the temperature effect. In Table 3 the calculated values of ΔOH for the reactions a–c, e–k are given. The variation of the coordinated OH oscillators is within a small range of 2–3 OH oscillators. Performing the reaction in D_2O enables one to calculate the number of coordinated water ligands for the initial and final reaction mixture by the empirical relation used by Horrocks and Albin [10].

$$q=1.05(P_{av,H_2O}-P_{av,D_2O}) \qquad (4)$$

This gives a number of 6.4 for the initial reaction mixture and 4 for the final one, resulting in a ΔOH of 2.4. This value is within the range found by the other method of calculation using eqn. (3) for reaction a.

The 'experimental' ΔOH values calculated from eqn. (3) for the ten experiments are plotted against the amount of cmos formed per amount of Eu(III) ion ($1/\rho_{cmos}$), wherein the amount of cmos formed is determined by HPLC (Fig. 6). A linear relation is obtained with a slope of 0.5. Apparently, an average of two OH oscillators are removed from the first coordination sphere when in a Eu(III)–ga–male mixed ligand system one male and ga are converted into one cmos per Eu ion. Both water and coordinated hydroxyl groups of alcohols are efficient quenchers of the $^5D_0$ excited state [10]. The decrease of two OH oscillators might originate from a water ligand that is released from the Eu(III) ion. However, an additional contribution of the coordinated hydroxyl group of ga, which is converted into a coordinated ether oxygen of cmos or which is released from the Eu(III) ion, is expected. It should be noted, however, that a full interpretation of the variation in the average number of OH oscillators per Eu requires detailed knowledge of the speciation in the solutions (initial and final) and the number of Eu–OH links in each of the species involved. Nevertheless, it may be concluded that the 'experimental' ΔOH per Eu(III) has been correlated to the ratio cmos/Eu ($=1/\rho_{cmos}$) for the final products of ten reactions corresponding to rather different conditions (pH, relative concentrations, temperature) with the relation $1/\rho_{cmos}=0.5\Delta OH\pm 10\%$. This correlation will hold for all the stages in the reaction within the error range indicated.

The plot in Fig. 6 can be used to determine the concentration of cmos in a reaction mixture from the $^5D_0$ lifetime, which is, evidently, a rather good

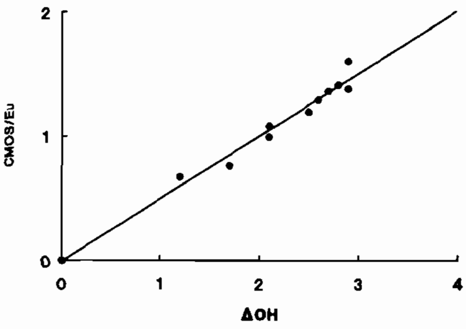

Fig. 6. Plot of the calculated change of the amount of water ligands in the first coordination sphere of Eu(III) as a function of the amount of cmos formed for reactions a–c and e–k (●), as given in Table 3.

method to monitor this reaction at its reaction temperature. In general, one may add that the luminescence–optical fiber setup cannot only be applied to this particular reaction, but also to the study of, for instance, the kinetics of the coordination of ligands to Eu(III), if the reaction is slow enough. The increase in lifetime of the $^5D_0$ excited state and the $^5D_0 \rightarrow {}^7F_0$ transition provide the tools for studying these reactions by luminescence.

Conclusions

It has been demonstrated that the luminescence–optical fiber setup can be used to study reactions on-line in which fluorescent rare earth ions are involved. This has been done for the Eu(III) promoted O-alkylation of ga with male at 363 and 343 K by continuously monitoring the lifetime of the $^5D_0$ emitting level. It can be concluded that the conversion of male and ga to cmos decreases the average number of OH oscillators by two in the Eu(III) coordination sphere if one cmos per Eu(III) is formed, which is translated into a higher lifetime of the $^5D_0$ excited state. Moreover, a linear relation was established between the observed variation in lifetime and the amount of cmos formed, which enables one to calculate the amount of cmos formed at the reaction temperature based on the lifetime of the $^5D_0$ emission of the reaction mixture.

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