

Photolysis of $\text{Zn}(\text{8-quinolinolate})_2(\text{H}_2\text{O})_2$ in non-aqueous solution. Photoactivation of hydrolysis



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ARTICLE INFO

Article history:

Received 10 March 2014

Accepted 11 April 2014

Available online 21 April 2014

Keywords:

Photochemistry

Hydrolysis

Zinc complexes

8-Quinolinolate complexes

ABSTRACT

The octahedral complex $\text{Zn}(\text{8-quinolinolate})_2(\text{H}_2\text{O})_2$ in non-aqueous solvents (e.g. chloroform, cyclohexane) undergoes a photolysis: $\text{Zn}(\text{8-quinolinolate})_2(\text{H}_2\text{O})_2 \rightarrow \text{Zn}(\text{OH})_2 + 2 \text{ 8-quinolinol}$. It is suggested that this photohydrolysis is facilitated by hydrogen bonding. The irradiation ($\lambda > 340 \text{ nm}$) is absorbed by the ligand chromophore. The IL excitation is associated with a charge shift from the coordinated phenolate to the nitrogen of the pyridine ring. As a consequence, the phenolate loses its coordinating ability. The subsequent deactivation is accompanied by the reversal of the charge shift. The regenerated phenolate may now undergo protonation from an adjacent water ligand in competition with the re-coordination to Zn^{2+} . This system represents a simple model for activation of water which is coordinated to zinc(II). In distinction to the enzymatic function the hydrolysis in our system is initiated by a light switch.

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Zinc enzymes play a very important role in a variety of biological processes [1]. They catalyze, for example, the hydrolysis of peptides (carboxypeptidase) or the reversible hydration of carbon dioxide (carboanhydrase). In these reactions water coordinated to zinc is activated (Eq. (1)).



Mechanistic studies are made more difficult by the lack of simple probes. Unfortunately, suitable chromophores as indicators generally are not available. While the catalytic function of hydrolases is based on thermal processes, proper models could be operated photochemically. Accordingly, such a photo-induced function would be stimulated by a light switch [2]. As a suitable model for an artificial photohydrolase we selected the complex $\text{Zn}(\text{oxinate})_2(\text{H}_2\text{O})_2$ (structure (1)) with oxinate = 8-hydroxyquinolinolate.

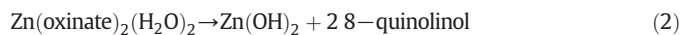
Oxinate complexes have been utilized for the qualitative and quantitative analysis of metal ions for many decades [3]. Moreover, the optical and photochemical properties of metal oxinates have been studied in quite some detail [4–8].

Irradiations were performed with a high-pressure mercury lamp Osram HBO W/2 as the light source. Monochromatic light was obtained by using Schott PIL/IL interference and Schott cutoff filters. Generally, the preparation of zinc oxinate is carried out in an aqueous medium [3, 9]. This leads to the formation of the aquo complex $\text{Zn}(\text{oxinate})_2(\text{H}_2\text{O})_2$ while its dehydration to $\text{Zn}(\text{oxinate})_2$ requires temperatures above

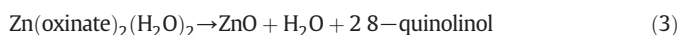
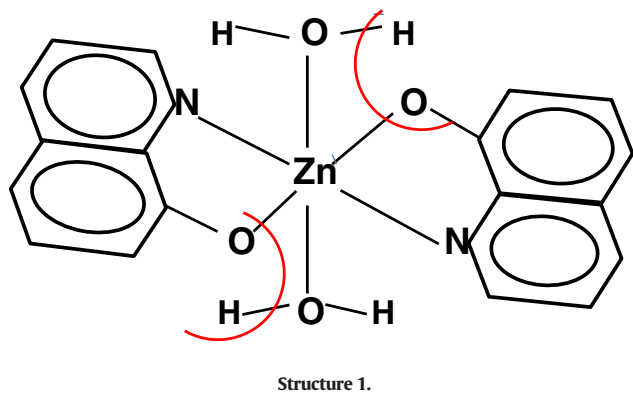
100 °C, e.g. 160 °C [9]. The aquo complex dissolves in various organic solvents. The compound is solvatochromic [3] since the excitation is associated with a charge redistribution in the oxinate ligands [4–8]. It is rather surprising that the aquo complex is soluble even in alkanes [10] but its solubility in all solvents is quite low [10]. The absorption and emission spectrum of $\text{Zn}(\text{oxinate})_2(\text{H}_2\text{O})_2$ in chloroform and cyclohexane (Fig. 1; absorption $\lambda_{\text{max}} = 345$ and 384 nm, emission $\lambda_{\text{max}} = 540$ nm) are rather similar.

The irradiation of these solutions with $\lambda > 320 \text{ nm}$ leads to the disappearance of the complex as indicated by the loss of its absorption, e.g. in CHCl_3 (Fig. 2). A rough estimate yielded a quantum efficiency of approximately $\phi = 10^{-3}$ at $\lambda_{\text{irr}} = 436 \text{ nm}$. At later stages of the photolysis the solution becomes cloudy. Colloidal particles cause the scattering of light which leads to an increase of the optical density over the whole UV/visible spectrum growing towards shorter wavelengths. When the photolysis is carried out in cyclohexane, the solution becomes cloudy already at the beginning of the irradiation. The photolysis can be driven to completion. After standing overnight the colloidal particles separate as a solid. The residual colorless and transparent solution shows only the absorption spectrum of 8-quinolinol with $\lambda_{\text{max}} = 245 \text{ nm}$; $\epsilon = 5 \times 10^4$ and 320 nm; $\epsilon = 3 \times 10^3$ [11]. The solid residue was dissolved in very little hydrochloric acid and upon addition of 8-quinolinol in ethanol transformed to zinc oxinate as indicated by its absorption spectrum. It is assumed that the colloidal particles and the final solid residue consist of ZnO or $\text{Zn}(\text{OH})_2$.

These observations lead to the conclusion that the photolysis proceeds according to the Eq. (2) or (3).



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Generally, zinc(II) complexes are not light sensitive because electronic excitation does not involve transitions with the participation of metal-based molecular orbitals since the $3d^{10}$ shell is too low and the empty $4s$ and $4p$ orbitals are too high in energy. Accordingly, the photosensitivity of zinc(II) complexes depends on the presence of suitable ligands. They should provide chromophores in the UV/vis region and luminescent and/or reactive intraligand (IL) excited states. The complex $\text{Zn}(\text{oxinate})_2(\text{H}_2\text{O})_2$ represents a rather intriguing case of this type.

The yellow fluorescence of $\text{Zn}(\text{oxinate})_2(\text{H}_2\text{O})_2$ (Fig. 1) is of the oxinate IL type and a characteristic feature of many oxinate complexes [4,6–8]. However, the photoreaction (Eq. (1)/(2)) is apparently a competing process of deactivation of this IL excited state. It can be rationalized by the following considerations. In reality, the IL excitation of oxinate is accompanied by a charge shift from the phenolate oxygen to the pyridine moiety [5,6,8,12]. In this ILCT state the coordinating ability of the phenolate function is lost and phenolate is then detached from zinc. The subsequent deactivation involves a reversal of the initial charge shift and hence a regeneration of the phenolate function. This in turn, may lead to the re-coordination of the phenolate to zinc, but as a competing process the phenolate abstracts a proton. The resulting oxinateH (8-quinolinol) is finally released. Since this photoreaction takes place in non-aqueous solution, the proton, which is transferred to the phenolate oxygen, must originate from the coordinated water ligands. This should be facilitated by the adjacent location of the proton donor and acceptor site (structure (1)) as confirmed by X-ray analysis [13,14]. Moreover, it seems likely that in the ground state this close approach is also favored by hydrogen bonding as marked in structure (1). While this photolysis seems to be a unique photoreaction, there are precedent cases which involve ligand substitutions as a consequence of the loss of coordinating ability induced by an ILCT excitation [15,16]. In this

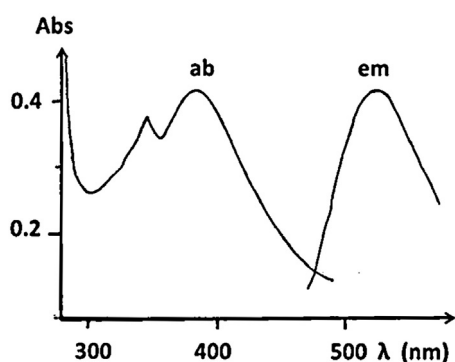


Fig. 1. Absorption (ab) and emission (em) spectrum of a 10^{-4} M $\text{Zn}(\text{oxinate})_2(\text{H}_2\text{O})_2$ solution in cyclohexane, 1-cm quartz cell, r.t., emission intensity in arbitrary units.

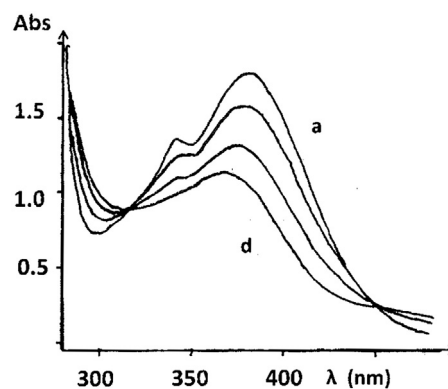


Fig. 2. Spectral variations during the photolysis of 4×10^{-4} M $\text{Zn}(\text{oxinate})_2(\text{H}_2\text{O})_2$ in chloroform at r.t., 1-cm quartz cell, $\lambda_{\text{irr}} > 320$ nm, irradiation time: (a) 0 min, (d) 12 min.

context, it might be suspected that it is simply the amount of energy which facilitates this photolysis. However, when the complex is heated up to 200°C , it loses only the water ligands under formation of $\text{Zn}(\text{oxinate})_2$ indicating that the photolysis is a quite selective process which is determined by the nature of the reactive excited state. In this case, it can be only of the IL (or ILCT) type [17]. At this point, it should be mentioned that biologically active ligands which are related to 8-quinolinolate are apparently coordinated to Zn^{2+} in natural systems [18].

In conclusion, we observed a photochemical hydrolysis: $\text{Zn}(\text{8-quinolinolate})_2(\text{H}_2\text{O})_2 \rightarrow \text{Zn}(\text{OH})_2 + 2 \text{ 8-quinolinol}$. This rather interesting example of photoactivation of a water ligand coordinated to Zn(II) is based on a charge shift induced by IL excitation of the quinolinolate ligand. This observation can be viewed as a photochemical analog of thermal hydrolysis as catalyzed by zinc enzymes in nature. Although our observations are based on a very simple system, they may stimulate more studies in this research field.

Acknowledgement

Financial support by DFG (grant Vo 211/19-1) is greatly appreciated.

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