

Photoproperties of silver sulfadiazine

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Abstract

Dry silver sulfadiazine (AgSD) is not light sensitive but shows a greenish-blue r.t. photoluminescence at $\lambda_{\text{max}} = 482$ nm which is suggested to originate from an IL triplet. In the presence of water AgSD undergoes a partial hydrolysis with the formation of free sulfadiazine (HSD) which has been previously shown to be photoreactive. Moreover, irradiation of an aqueous suspension of AgSD leads also to the photoreduction of Ag^+ to elemental silver. This photolysis might explain the origin of argyria which can occur when AgSD in contact with human skin is exposed to sun light

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Silver sulfadiazine (AgSD) is a commercial product (e.g. Aldrich) which is applied for the therapy of injured skin, in particular burns. The activity of AgSD is based on its bacteriostatic properties. AgSD consists of deprotonated sulfadiazine SD^- and Ag^+ which has replaced the imido proton of HSD [1]. Sulfadiazine (Structure 1) belongs to a group of sulfonamides which have been used for decades to fight infections. Unfortunately, the increase of antibiotic resistance is a serious problem. In this context silver ions play an important role [2,3]. For centuries it has been known that silver and silver compounds are rather effective for the prevention and treatment of infections in general. The renewed interest in silver compounds as antibacterial agents has been highlighted in two very recent feature articles [4,5]. It follows that the presence of the two active ingredients, silver as well as sulfadiazine, should enhance the benefit of AgSD.

However, it has been emphasized that the exposure of skin treated with AgSD to sun light should be avoided in order to prevent argyria. A corresponding warning is included in the user information of commercial burn treat-

ment creams which contain AgSD (see e.g. Flammazine, Solvay). Argyria is an irreversible skin darkening which is caused by the deposition of elemental silver and possibly silver sulfide. Accordingly, the study of the excited state behavior of AgSD should be of considerable interest. Moreover, irrespective of its medical significance the examination of the photoproperties of AgSD is also of interest in a quite different context. Generally, the luminescence of silver complexes has attracted much attention in recent years [6]. Frequently, the emission seems to originate from the ligands, but the function of the silver ions is not yet really clear in most cases.

Without decomposition AgSD is not soluble in common solvents. Dry AgSD shows a greenish-blue luminescence. At 77 K the emission spectrum (Fig. 1) shows a band at $\lambda_{\text{max}} = 470$ nm with a vibrational structure. At r.t. this spectrum is very similar ($\lambda_{\text{max}} = 482$ nm) but the structural features are blurred. The excitation spectrum (Fig. 1) exhibits two maxima at 243 and 352 nm. The emission and excitation spectrum show one common shoulder at approximately 415 nm. For comparison, the emission spectrum of HSD was also recorded. HSD is nonfluorescent [7], but emits a phosphorescence in low-temperature glasses at $\lambda_{\text{max}} = 410$ nm [7,8]. The structural features (Fig. 2) are reproducible.

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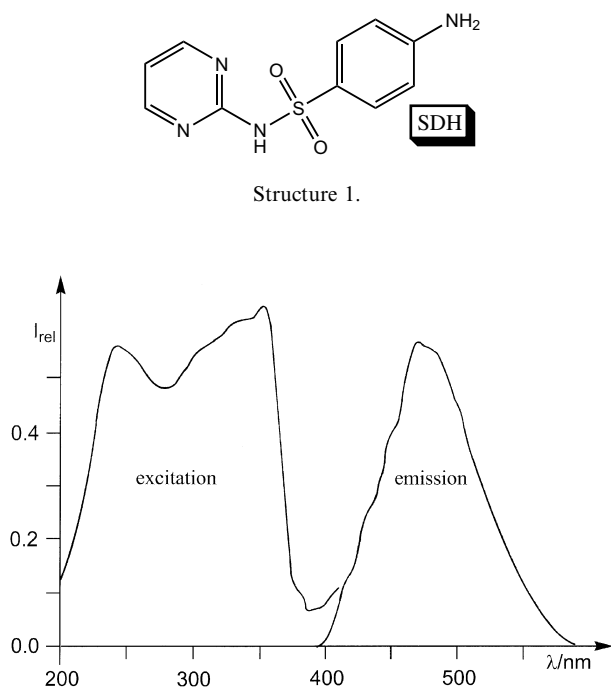


Fig. 1. Electronic excitation ($\lambda_{em} = 480$ nm) and emission ($\lambda_{exc} = 300$ nm) spectrum of solid silver sulfadiazine at 77 K, intensity in arbitrary units.

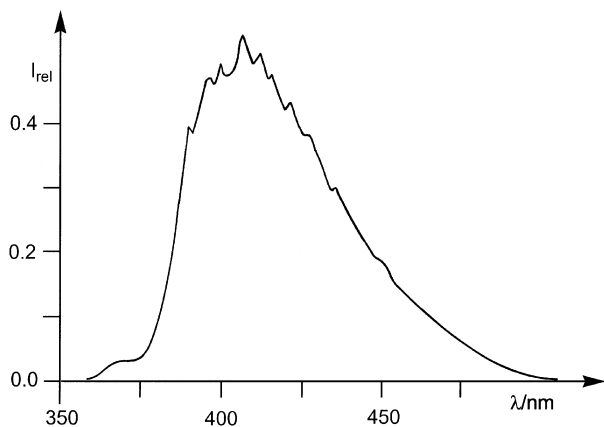


Fig. 2. Electronic emission ($\lambda_{exc} = 280$ nm) spectrum of sulfadiazine in EtOH at 77 K under argon, intensity in arbitrary units.

Dry AgSD is rather light stable. A suspension of AgSD in various solvents which contain small amounts of water apparently undergoes some hydrolysis ($2\text{AgSD} + \text{H}_2\text{O} \rightarrow \text{Ag}_2\text{O} + 2\text{HSD}$) as indicated by the spectrum of the filtrated suspension. This spectrum is essentially identical to that of pure HSD with $\lambda_{max} = 267$ nm (Fig. 3). Irradiation of this solution is accompanied by very clean spectral changes including new maxima at 297, 246 and 225 nm and isosbestic points at $\lambda = 296, 253, 221$ and 207 nm. A tentative analysis of these changes seems to indicate the occurrence of a photohydrolysis of the sulfonamide: $\text{HSD} + \text{H}_2\text{O} \rightarrow 2\text{-aminopyrimidine}$ ($\lambda_{max} = 297$ and 227 nm) [9] + sulfanilic acid ($\lambda_{max} = 249$ nm) [10]. However, in a recent study it was revealed that the photolysis of

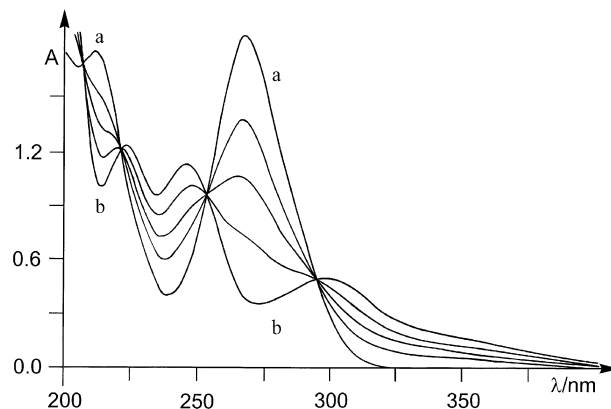


Fig. 3. Spectral changes during the photolysis of 1.03×10^{-4} M sulfadiazine in a mixture of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (99:1) at room temperature after 0 min (a), 0.5, 1, 2 and 4 min (b) irradiation times with white light (Osram HBO 200 W/2 lamp), 1-cm cell.

HSD is associated with the extrusion of SO_2 and the concomitant formation of 4-(2-iminopyrimidine-1(2H)-yl)-aniline as stable photoproduct [11]. When an aqueous suspension of AgSD is photolyzed ($\lambda_{irr} = 254$ or 366 nm) and then filtered, the solution spectrum shows features which are similar to those of the photolyzed solution of HSD, but in addition some colloidal silver has apparently been generated. An inflection at approximately 406 nm indicates the appearance of the characteristic plasmon absorption of colloidal silver [12].

AgSD is an insoluble compound which consists of polymeric chains [1]. Two such chains form a double stranded structure which contains pairs of Ag^+ cations in relatively close contact (2.916 Å). The configuration at the silver ions is a distorted trigonal bipyramid. Silver is coordinated to a deprotonated amide nitrogen, to a sulfonyl oxygen, and a pyrimidine nitrogen in the same chain. In addition, each silver is coordinated to a further pyrimidine nitrogen and silver ion of the neighbour chain.

The Ag^+ ion is characterized by a MC $4d \rightarrow 5s$ transition at relatively high energies. The longest-wavelength ds absorption of Ag^+ complexes appears near 250 nm [13]. However, in compounds with short silver–silver distances ds excited states may be shifted to lower energies but the corresponding emission bands have not been observed to show a structure [13]. Since Ag^+ is only a rather weak CT acceptor LMCT transitions of silver complexes do not occur at long wavelength [14]. On the other hand, Ag^+ is a CT donor [15,16] and pyrimidine a CT acceptor [17], but only of moderate strength. From these considerations it follows that the MC, LMCT or MLCT transitions of AgSD are expected to occur only at rather high energies. We suggest that the emission of AgSD at 482 nm originates from the lowest IL triplet. This assignment is supported by several observations. First of all, the free ligand HSD shows its phosphorescence (Fig. 2) at a wavelength comparable to the luminescence of AgSD (Fig. 1). In addition, both emissions display a vibrational structure. Since silver

is able to induce a heavy-atom effect in ligands [6] the IL phosphorescence of AgSD does not only appear at low temperatures but also under ambient conditions. The 415 nm shoulder which shows up in the excitation and emission spectrum of AgSD is assumed to belong to the 0–0 transition. Although it is rather pronounced in the excitation spectrum it should be rather weak in absorption because AgSD is nearly colourless. Its low intensity agrees with the spin-forbidden character of this IL transition.

Generally, solid metal complexes are rather light stable. Nevertheless, CT excitation can lead to an initial electron transfer. However, the rigid structure of the lattice favours back electron transfer and thus prevents product formation. In contrast, in solution or at the interface between the solid and a suitable solvent the irreversible formation of photoproducts can take place since it is facilitated by diffusion. This could explain the generation of colloidal silver upon irradiation of an aqueous suspension of insoluble AgSD. The photoreduction of Ag^+ is well known [12]. In molecular compounds it is induced by LMCT excitation. We suggest that this applies also to AgSD and its hydrolysis products. In contrast, dry AgSD is light stable and irradiation leads only to an emission from the lowest-energy IL triplet which must be located below the reactive LMCT state.

In summary, while dry AgSD is not light sensitive it shows an IL phosphorescence. Although AgSD is insoluble in common solvents without decomposition it is light sensitive in contact with water. The photolysis of an aqueous

suspension of AgSD leads to the formation of elemental silver. This photoreaction may cause argyria upon exposure of AgSD on human skin to sun light.

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