

Kinetics and mechanism of the photochromic transformations of *N*-salicylidene-4-hydroxy-3,5-dimethylaniline and its complex with uranium(VI) dioxide

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Abstract

The title compounds were prepared and some of their photophysical and photochemical properties studied. The anil (LH) and its complex with uranium (C) were found to possess very similar spectral and kinetic characteristics, namely absorption and luminescence spectra, photoisomer spectra and isomerization kinetics. From these measurements, it is concluded that the photoexcitation of the compounds in polar solvents (methanol and acetonitrile) leads to proton transfer in the excited singlet state with the formation of a trans zwitterionic structure. The trans zwitterion emits light and undergoes isomerization to form the cis zwitterion. The latter compound is a photochromic intermediate, which participates in cis–trans isomerization (rate constant $k_{iso} = (3-4) \times 10^4 \text{ s}^{-1}$) with the formation of the initial anil or the uranyl complex. An energy-level scheme of the reactions is presented.

1. Introduction

Photochromism is an active field of research in photochemistry because of its actual and potential applications [1]. Knowledge of the precise reaction mechanisms of photochromic reactions is of interest because such knowledge enables the development of methods to control the reaction rates and quantum yields of products. Compounds of different classes, and in particular anils of salicylaldehydes, are currently under study as photochromic materials [2]. Two important general problems in the photochromism of anils are the mechanism of photochromic action and the structure of photochromic intermediates [2].

Two different viewpoints exist concerning the mechanism of photochromism of anils of salicylaldehydes (Fig. 1): one photochromic mechanism involves a hydrogen atom transfer with formation of the cis and trans keto isomers as photochromic intermediates [2–4], and the other mechanism involves, a hydrogen ion transfer with the formation of cis and trans zwitterionic isomers as photochromic intermediates [2, 5, 6]. The present research aims to provide experimental information which will assist

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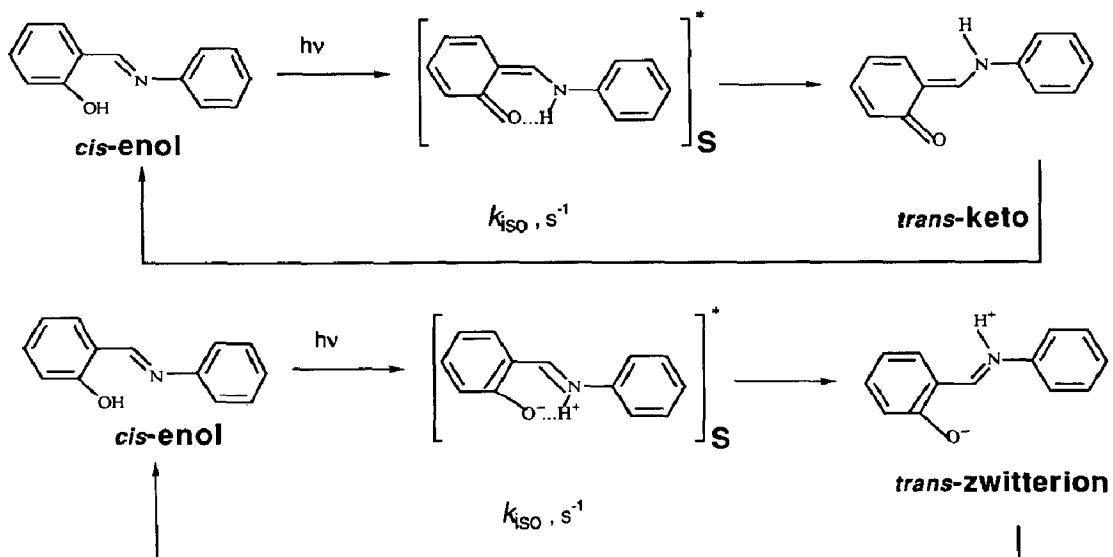
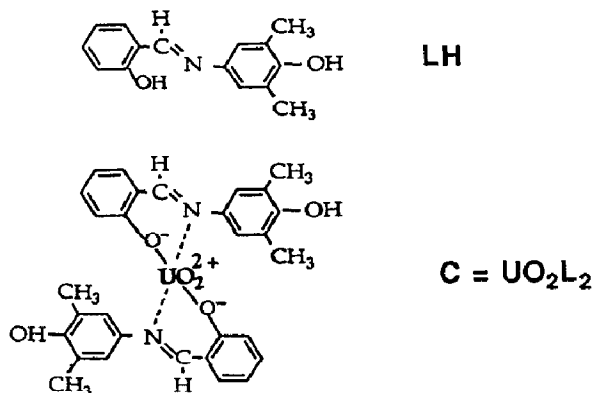


Fig. 1. Proposed reaction schemes for photochromism of salicylaldehydes. Top: enol-keto isomerization with the keto form being the transient photochromic species. Bottom: isomerization to *cis* and *trans* zwitterion with the *trans* zwitterion being the transient photochromic species [2-6].

in investigating this mechanistic problem. For this purpose, the novel photochromic compounds of anils of salicylaldehydes (Scheme 1), namely *N*-salicylidene-4-hydroxy-3,5-dimethylaniline (LH) and its complex (C) with uranium(VI) dioxide (UO_2L_2), have been synthesized and studied.



Scheme 1. Structures of LH and C.

2. Experimental details

The compounds LH and C (Scheme 1) were synthesized and purified according to a literature procedure [7, 8]. In particular, C was prepared in aqueous alkaline solution at approximately 340 K in an inert atmosphere (argon) from LH according to the reaction



The yield of C was 73%. In the absence of base a different complex of uranyl and LH is formed. Solutions of LH and uranyl sulfate in methanol show a drastic increase in optical density in the visible region compared with the sum of the absorbances of the individual compounds at the same concentrations; this is due to the formation of a complex (N) of LH and UO_2SO_4 (eqn. (2)), which is different from C. The most probable value of x in eqn. (2) is unity [9].



Benzophenone (Aldrich) was recrystallized from ethanol. Acetonitrile, methanol and uranyl sulfate ($\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$) (all reagent grade, Fisher) were used as received.

IR spectra ($50\text{--}4500\text{ cm}^{-1}$) of LH and C were recorded as Nujol mulls between KBr plates on a single beam Fourier transform IR (FT-IR) Perkin-Elmer 1600 spectrometer at 2 cm^{-1} resolution and strong apodization. Proton nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AF 250 MHz instrument with Me_4Si as internal standard. For NMR experiments the solvents CD_3OD (Fluka) and CD_3CN (Aldrich) were employed. UV-visible absorption spectra were recorded on a Varian Cary-219 absorption spectrophotometer. Emission spectra were measured on a Perkin-Elmer LS-5 fluorescence spectrometer. Nanosecond excimer laser flash photolysis ($\lambda_{\text{ex}} = 308\text{ nm}$) and microsecond lamp flash photolysis, described in refs. 10 and 11, were employed. Time-resolved absorption and emission measurements were performed using an OMA system described elsewhere [10]. The spectra were averaged for about 15 laser shots. Lamp flash photoexcitation was performed through light filters in the region $\lambda = 280\text{--}380\text{ nm}$. Samples were deoxygenated by prolonged argon bubbling. All experiments were performed at room temperature.

3. Results and discussion

The anil LH is soluble in polar and non-polar solvents. It is insoluble in water at room temperature. The complex C was found to be soluble in methanol, acetonitrile, *N,N*-dimethylformamide and pyridine. Uranyl complexes of similar structure are well known [9]. Evidence for the complex derives from the following spectroscopic information.

The IR spectra (Nujol mulls) of LH and C are similar. However, two readily observed differences in the spectra are indicative of the existence of a complex. First, an intense absorption at $\nu = 897\text{ cm}^{-1}$ does not appear in the spectrum of LH or $\text{UO}_2(\text{NO}_3)_2$, but is present in the spectrum of C. This absorption is assigned to an antisymmetric O=U=O stretch of the uranyl moiety [9, 12]. Second, absorption in the spectral region of $\nu = 1610\text{--}1630\text{ cm}^{-1}$ corresponds to C=N vibrations in both compounds. Most convincingly, there is an observed increase in ν from 1618 cm^{-1} in LH to 1628 cm^{-1} in C which is assigned to an increase in C=N bond order due to complexation [12].

^1H NMR spectra of LH and C solutions show direct evidence for the existence of a complex in solution. The spectra of LH and C in acetonitrile exhibit ^1H signals for methyl groups at $\delta = 2.2$, aromatic protons at $\delta = 6.8\text{--}7.5$, OH of the 4-hydroxyl group at $\delta = 6.25$ and azomethine (CH=N) at $\delta = 8.55$ (LH) and $\delta = 8.51$ p.p.m. (C). Rather similar spectra are observed in methanol with the following differences: no OH group signals are observed due to the fast exchange with methanol; the azomethine protons have signals at $\delta = 8.74$ (LH) and $\delta = 8.41$ p.p.m. (C). It has been reported

that complex formation with uranyl alters the electronic shielding of protons positioned in the vicinity of ligand atoms, which form bonds with UO_2^{2+} , and the magnetic anisotropy of the uranyl group is the most important factor causing changes in the chemical shift of the protons [13].

Figure 2 shows the absorption and emission spectra of LH and C in methanol. The fluorescence maximum (520 nm, $19\,230\text{ cm}^{-1}$) is shifted over 9000 cm^{-1} to the red compared with the absorption maximum (350 nm, $28\,570\text{ cm}^{-1}$). Such large Stokes' shifts are well documented for anils of salicylaldehydes and have been ascribed to singlet excited state emission from a keto tautomer [2–4] or a zwitterion [2, 5, 6]. Fluorescence spectra obtained by time-resolved laser photolysis or steady state spectrofluorometry have the same shape and luminescence maxima within experimental error ($\pm 5\text{ nm}$).

The absorption and luminescence spectra of LH and C are also very similar (Fig. 2). However, the absorption and luminescence spectra of C are quite different from those of uranyl salts of mineral acids and, in particular, UO_2SO_4 . The latter compound in methanol displays several absorption bands in the region $\lambda=360\text{--}480\text{ nm}$, with the most intense maximum at $\lambda=421\text{ nm}$, and an emission spectrum with maxima at 455 and 485 nm on excitation at $\lambda=400\text{--}430\text{ nm}$ (Fig. 2).

The absorption spectrum of C mainly exhibits features of LH, and uranyl absorption is not detectable. This is not surprising because the UO_2^{2+} extinction coefficient in the visible region is very weak: $\epsilon_{\text{max}}=35\text{ M}^{-1}\text{ cm}^{-1}$ and $\epsilon=21\text{ M}^{-1}\text{ cm}^{-1}$ at $\lambda=350\text{ nm}$ (UO_2SO_4 in methanol, Fig. 2). The absorption of C at $\lambda=350\text{ nm}$ is characterized

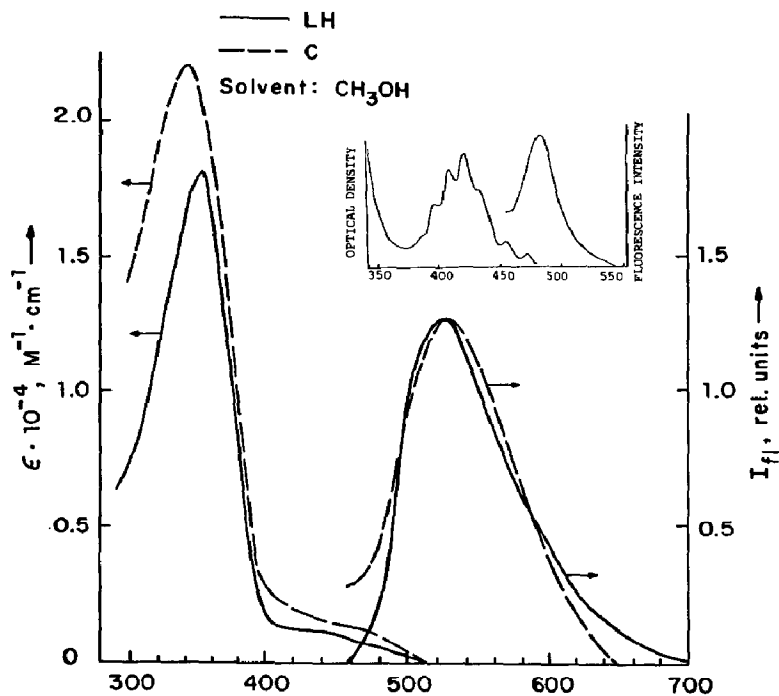


Fig. 2. Absorption and fluorescence spectra of LH (full lines) and C (broken lines) in methanol. Fluorescence intensity is presented in relative units. For fluorescence measurements, solutions of $3 \times 10^{-5}\text{ M}$ of LH and C were used with excitation at $\lambda=350\text{ nm}$. Similar spectra are obtained in acetonitrile. Inset: absorption and luminescence spectra of uranyl sulfate in methanol.

by a hyperchromic effect relative to LH (Fig. 2), which may be expected in view of the presence of two LH moieties in the complex. The absorption of UO_2^{2+} in the visible region may be considered to undergo a hypsochromic shift to the UV region but is not observable. The stability of uranyl complexes with organic ligands has been found to be proportional to the value of such hypsochromic shifts [14]. In fact, the complex seems to be very stable towards dissociation of ligand and uranyl. Thus, the addition of concentrated acetic acid to a solution of C in methanol or acetonitrile does not lead to the expected acid-induced dissociation (eqn. (3)), because both the absorption and luminescence spectra of C are not changed by the addition of strong acid



(If reaction (3) did occur we would observe a decrease in absorption at 350 nm or the appearance of complex N (eqn. (2)) absorption). However, the dissolution of C in concentrated nitric acid leads to the appearance of the characteristic bands of UO_2^{2+} luminescence, such as the intense luminescence bands at $\lambda = 490$ and 515 nm, which characterize the emission of uranyl salts in strong acidic aqueous solutions [15].

Transient absorption spectra obtained by laser or lamp flash photolysis of LH and C were very similar ($\lambda_{\text{max}} = 485 \pm 5$ nm, Fig. 3). The relatively slow decay of this transient(s) obeyed first-order kinetics and the starting material was regenerated. The regeneration of the starting material suggests that the transient(s) is an isomer of LH (C) (*cf.* refs. 2-6). Two suggested structures of these transients are presented in Fig. 4. The measured rate constants of isomerization to regenerate the starting material in methanol are $k_{\text{iso}} = (3.5 \pm 0.5) \times 10^4$ and $(4.0 \pm 0.5) \times 10^4 \text{ s}^{-1}$ for LH and C respectively. Air (oxygen) does not influence the isomerization kinetics. We now consider evidence for the identity of the structure (Fig. 1) of these isomeric transients.

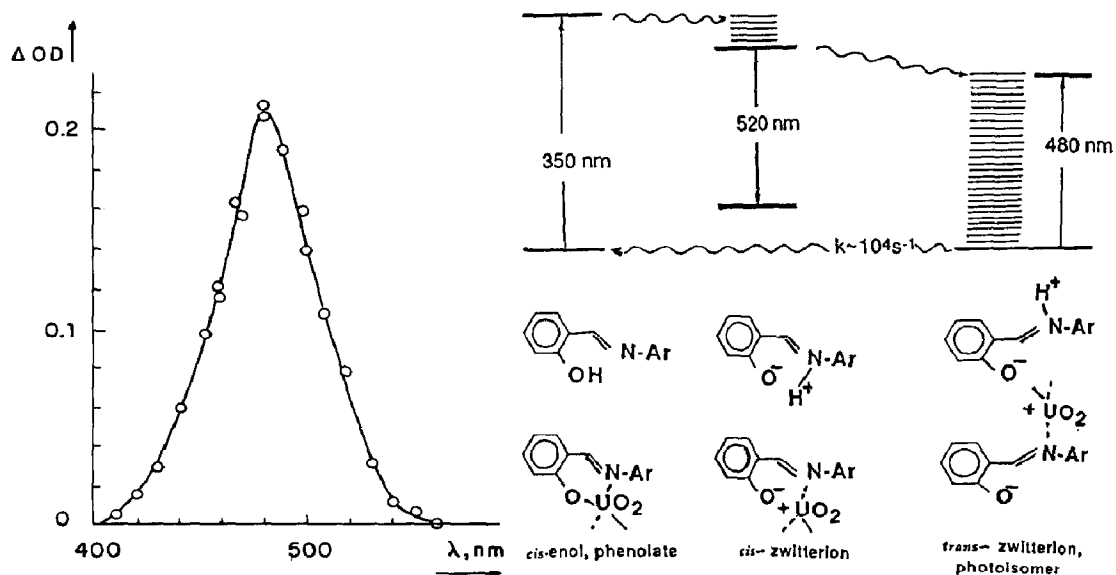


Fig. 3. Absorption spectrum of photoisomer of C (obtained during lamp flash photolysis of C (5×10^{-5} M) in methanol). Spectrum obtained at 50 μs after the flash.

Fig. 4. Energy-level diagram of main photoreactions and dark reactions of LH and C in polar solvents.

Photoexcitation of benzophenone (BP) in acetonitrile leads to the formation of triplet BP_T^* (absorption maximum at $\lambda=520$ nm [16]). The decay of BP_T^* follows first-order kinetics with a rate constant k_0 of $(1.8 \pm 0.5) \times 10^5$ s⁻¹. The addition of LH to the solution in concentrations up to 3×10^{-4} M leads to the acceleration of BP_T^* decay and the appearance of a transient absorption with a maximum around $\lambda=545$ nm, which may be ascribed to a ketyl radical $BPH\cdot$ formed through hydrogen atom (electron) transfer



Since LH is a substituted phenol, triplet benzophenone abstracts a hydrogen (electron) from it at a high rate [16, 17]. The estimated k_4 value is $(1.0 \pm 0.3) \times 10^{10}$ M⁻¹ s⁻¹, so that reaction (4) seems to be diffusion controlled. A small acceleration of BP_T^* decay in the presence of C has also been observed; in a saturated solution of C in acetonitrile (4×10^{-5} M) the rate constant of BP_T^* decay was $(3.5 \pm 0.5) \times 10^5$ s⁻¹, which is smaller than the first-order rate constant of BP_T^* decay in the presence of LH and C at the same concentration is further evidence for complex formation.

The isomerization rate constants are comparable with the rate constants reported previously for a number of substituted *N*-salicylideneanilines in non-viscous solvents ($k \approx 10^3$ – 10^4 s⁻¹) [4], but are 4–5 orders of magnitude larger than the isomerization constants of 4,4'-disubstituted *N*-benzylideneanilines [18]. Isomerization of *N*-salicylideneanilines is accompanied by restoration of the O–H bond in the salicylaldehyde fragment; this bond formation leads to significant energy gain, a relatively small activation barrier and larger rate constants.

4. Conclusions

Figure 4 summarizes the results. The striking feature of the compounds C and LH is the similarity of their spectral and kinetic characteristics, *i.e.* absorption and luminescence spectra, photoisomer spectra and isomerization kinetics. This enables us to conclude that the elementary reactions of photoexcited C and LH are quite similar and the intermediates have, in principle, similar structures. Complexation does not reduce the lability of the ligand moiety to undergo isomerization in the excited state. However, the photoexcited C molecule cannot form the *cis* keto isomer (see Fig. 4). In fact (substituted) phenolate (negatively charged ion) cannot isomerize into the uncharged keto form in any fast elementary reaction. Phenolate can only be oxidized into the phenoxyl radical; the bimolecular reaction between two phenoxyls leads to the formation of keto structures, but this is obviously unlikely in the present case.

It is known that hydroxyl-substituted aromatic compounds become much more acidic in the singlet excited state [19] and it is quite reasonable that photodissociation occurs, and that the zwitterionic molecule is formed after excitation of anils of salicylaldehydes. Thus, we conclude that the photoisomerization occurs via proton transfer at least in polar solvents [5, 6]. This claim was made in the pioneering publications of Weller [19, 20], who studied the photochemistry of methyl salicylate and concluded that a large fluorescence Stokes' shift is related to proton transfer.

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