

Articles

Photochemical Studies of Schiff Base Cu(II) Complex: (1) UV-Irradiation of *N,N'*-bis(salicylidene)ethylenediamine copper(II)

Byung-Tae Ahn

Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea

Received August 10, 1994

The ultraviolet photochemistry of *N,N'*-bis(salicylidene)ethylenediamine copper(II), Cu(sal)₂en, was investigated with low pressure mercury lamp. Reduction of Cu(II) and formation of Cl⁻ were shown on 254 nm irradiation both for aerated and deaerated chlorinated hydrocarbon solvent such as CH₂Cl₂, chloroform, and 1,2-dichloroethane. Relatively long lived ($\tau=100$ μ sec) intermediate was detected by flash photolysis. Overall photo-process can be described as the formation of Cl⁻ and new copper complex, product(1) by chlorohydrocarbon mediation, photoinduced reduction by abstraction of halogen from solvent, followed by redox induced substitution of axial ligand with chlorine. Product(1) is possibly Cu(III) chlorosalicylaldehydeimido complex and cyclic -CH₂CH₂- moiety is absent in the structure. 247 nm band of Cu(sal)₂en should contain ligand to metal charge transfer character.

Introduction

Schiff-base ligand complexes have gained lots of interests mainly due to their ease of preparation, their diverse properties and their use as biological models. But very few photochemical studies were reported.¹ Our interest in the photochemical reactivity of the Schiff-base complexes of copper has led us to investigate *N,N'*-bis(salicylidene) ethylenediamine copper(II), Cu(sal)₂en, particularly due to the stability in most organic solvents. Absorption spectrum shows three different types of bands, *i.e.* d-d band at 562 nm, ligand band at 356 nm and 272 nm, and complicated band at 247 nm.^{2,3} Photochemistry by 254 nm uv light irradiation with low pressure mercury lamp is reported.

Experimental

Materials. Cu(sal)₂en was prepared by literature method.⁴ UV-visible spectral profile and molar absorptivity were agreed well with the literature values.^{2,4} Glass distilled CH₂Cl₂, spectral grade absolute ethanol (from Merck), and column distilled chloroform were used. All other materials were reagent grade quality. Ion exchange resin for cation was Sephadex 25-C (100-200 mesh) and that for anion was Amberlite IR-45 (Mallinckrodt).

Photolysis Procedures. Continuous irradiation were carried out in the cell of light path 1cm with side arm of 2 mm absorbance monitoring cell. The homogeneity of the reaction medium was maintained by stirring the solution with magnetic bar. For 254 nm irradiation, low pressure mercury lamp (Rayonet Photochemical Reactor Lamp, Cat. No. RPR-2537 A) was used. Approximately 0.3 mM solution of Cu(sal)₂en was irradiated in various solvent. The gaseous layer of irradiation cell was covered with aluminum foil to prevent the complication of possible gaseous reaction. For anaerobic studies the cells were purged with nitrogen gas prior to irradiation. The incident light intensity was deter-

mined by ferrioxalate actinometry.⁵ Stability of light intensity from time to time was checked by radio meter (Oriol model 7070).

Oxygen Intake Study. 8.00 mL of 3.00 mM of Cu(sal)₂en in CH₂Cl₂ was taken into the high vacuum stoppered quartz cell whose volume was approximately 12 mL. The solution was degassed by four times freeze-thaw cycling. To prevent the cracking of the cell, quick thawing was necessary. Known amounts of oxygen and nitrogen were introduced through the cell utilizing the vacuum line and the manometer. After the irradiation, the gas in the reaction cell was collected by Toefler pump and it was analyzed for O₂ and N₂ through gas chromatographic column (2A, molecular siever).

Flash Photolysis. The flash photolysis apparatus was described elsewhere.⁶ The instrument in Radiation Lab. (Notre Dame, IN) had been used.

Analysis of the Reaction Product. Approximately 200 mL of 3 mM concentration of Cu(sal)₂en in CH₂Cl₂ was irradiated with low-pressure mercury lamps housed in cylindrical drum at its center the quartz reaction flask was located (Rayonet lamp). Air stream was passed through the solution, and additional stirring was done with stirring bar. On several hours of irradiation reddish purple product was precipitated. After filtering, it was washed with CH₂Cl₂ several times. After air dry, the filtrate was washed again with ethanol, then vacuum dried. Gas chromatographic separation of possible gaseous product formed and determinations of the amount of oxygen consumed were tried.

Spectroscopic Measurements. UV-vis spectra were recorded on a Cary 210 (Varian Associates) or U-3210 (Hitachi) spectrophotometer. Infra-red spectra of the samples were taken as KBr pallets with a Perkin-Elmer Model 337 spectrophotometer. X-Band ESR spectra of Cu(sal)₂en and product (1) were recorded with a Varian spectrometer.

IR (KBr pallet): 1645 (s), 1629 (s), 1600 (s), 1449 (s), 1388 (w), 1347 (m), 1333 (m), 1305 (m), 1290 (m), 1280 (m), 1237 (m), 1191 (s), 1150 (m), 1125 (s), 1085 (m), 1050 (m), 1035

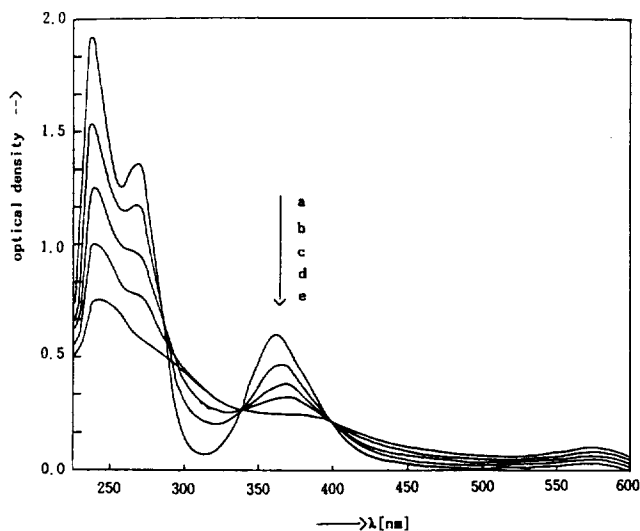


Figure 1. Absorption spectra of 0.5×10^{-4} M $\text{Cu}(\text{sal})_2\text{en}$ in deaerated CH_2Cl_2 on 254 nm Hg lamp irradiation. Irradiation time: (a) 0, (b) 4, (c) 8, (d) 12, (e) 16 min.

(m), 976 (m), 903 (m), 770 (m), 763 (m), 758 (m) cm^{-1} .

Elemental Determination. Chemical analysis for C, N, and H were done by Schwarzkopt Microanalytical Laboratory, New York, New York. Copper was determined by colorimetric method using 2,9-dimethyl-1,10-phenanthroline.⁷ Chlorine was determined by gravimetric method by forming AgCl . Anal. Calculated for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2\text{Cl}_2\text{Cu}_{2.5}\text{H}_2\text{O}$ C, 40.16; H, 3.85; N, 6.69; Cl, 16.93; Cu, 15.18. Found: C, 39.72; H, 4.30; N, 7.64; Cl, 16.9; Cu, 15.50.

Calculations. The spectral features of irradiation solution is the net result of absorptions of reactants and products formed. At the small fraction of reaction of early stage of irradiation, the absorbance change at 375 nm can be assumed to be from the loss of starting material $\text{Cu}(\text{sal})_2\text{en}$, because the molar absorptivity of $\text{Cu}(\text{sal})_2\text{en}$ is large when compared with other product. As the light absorbed at 254 nm in 1 cm light-path is much higher than 3, we can assume that all the incident light is absorbed by reactant $\text{Cu}(\text{sal})_2\text{en}$. Quantum yields for the disappearances of $\text{Cu}(\text{sal})_2\text{en}$ ($\Phi\text{-Cu}(\text{sal})_2\text{en}$) were calculated from the absorbance changes at 356 nm band and light intensity from actinometry.

Results and Discussion

Several hours of irradiation to $\text{Cu}(\text{sal})_2\text{en}$ in CH_2Cl_2 on medium pressure mercury lamp with 360 nm band pass filter doesn't change any spectral features at all. This indicates that this type of Schiff base copper(II) compound is photochemically stable on visible light irradiation. Spectral changes on 254 nm irradiation were observed only in solvent CH_2Cl_2 , chloroform, and 1,2-dichloroethane. When aluminum foil which was shielding gaseous layer was unwrapped after low pressure mercury lamp irradiation, whole compound became yellow precipitate which formed from the top of the solution. Further production of ionic molecule from the secondary reaction is suggestive from this process. Figure 1 is the typical absorption spectra change of $\text{Cu}(\text{sal})_2\text{en}$ on 254 nm low

Table 1. Relative quantum yield for the disappearance of $\text{Cu}(\text{sal})_2\text{en}$ in chlorinated solvents by UV irradiation

Solvent	³ Relative $\Phi\text{-Cu}(\text{sal})_2\text{en}$
CCl_4	—
CHCl_3	17.3
CH_2Cl_2	8.75
$\text{CH}_2\text{ClCH}_2\text{Cl}$	2.85
*3.75M CHCl_3 in EtOH	27.6
6.25M CHCl_3 in EtOH	43.6
8.75M CHCl_3 in EtOH	53.0
12.50M CHCl_3 in EtOH	87.7

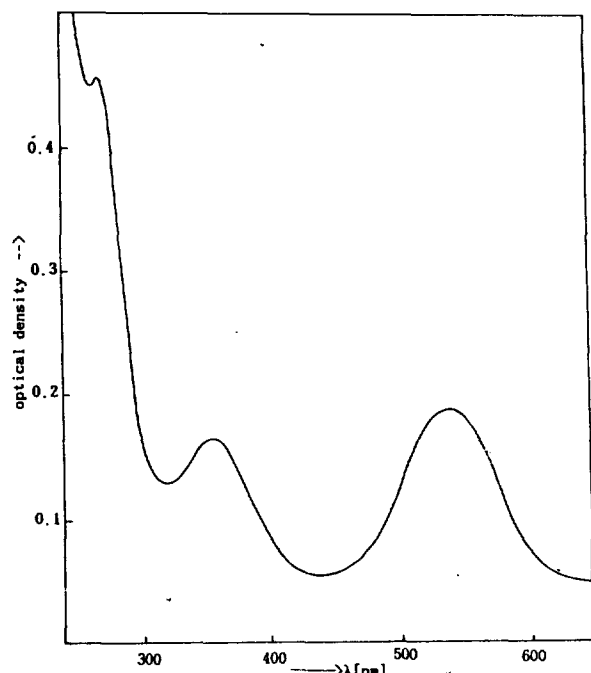
All of the initial concentrations of complex were 0.05 mM except *case where it was 0.3 mM.

pressure mercury lamp irradiation in deaerated CH_2Cl_2 solvent. Steady decrease in absorbance at 365 nm band and 275 nm band with two isosbestic points at 401 and 343 nm was seen. Formation of intermediate can be noticed by the increase of absorption maximum at around 440 nm by flash photolysis (vide infra). Although intermediate is soluble, copper compound of irradiation product(1) formed is insoluble in methylenechloride as seen by sharp two isosbestic points and final precipitation. The yellow precipitate became reddish purple in aerated chlorinated hydrocarbon solvent. No spectral change was seen in solvent ethanol, methanol, and acetonitrile. This is strong suggestion that the 5th or 6th coordination of Lewis base type of ligand to the copper center inhibits photochemical reaction. The quantum yields for the disappearance of $\text{Cu}(\text{sal})_2\text{en}$ were increased on the change of chlorinated solvents ($\text{CH}_2\text{ClCH}_2\text{Cl} < \text{CH}_2\text{Cl}_2 < \text{CHCl}_3$) and on increasing CH_2Cl_2 concentration in aerated ethanol solvent (Table 1). This is consistent with C-Cl bond strength of the different solvents. Passage of chlorine or ozone gas through the $\text{Cu}(\text{sal})_2\text{en}$ solution of CH_2Cl_2 didn't make any observable color change or the reaction of the solution. Therefore the redox reaction by direct oxidation due to possible product O_3 or Cl_2 is eliminated. Reddish purple product(1) formed in aerated CH_2Cl_2 was isolated and analyzed, vide supra. On adding ethanol solution of AgNO_3 to the irradiated solution of $\text{Cu}(\text{sal})_2\text{en}$ in deaerated CH_2Cl_2 solution, white silver chloride precipitate formed in contrast to the fact that no formation of the precipitate was seen on nonirradiated solution. Gas chromatographic analysis of gas layer of reaction cell showed the presence of the trace amount of some other molecules other than N_2 , and O_2 . This trace could be ethylene oxide molecule assumed from elemental analysis data of product(1). Elemental analysis and IR data fit well for the CH_2CH_2 detachment from $\text{Cu}(\text{sal})_2\text{en}$. Oxygen intake study showed the increased consumption of oxygen on longer irradiation and longer standing as shown in Table 2. At first step the oxygen in the solvent is not involved in the reaction. Spectral change of the irradiated solution on several days standing completed the formation of purple product(1). For anaerobic condition, we failed in getting an appreciable amount of product to do analysis due to low quantum yield and no isolable insoluble product. Isolated product dissolved in ethanol/water (50/50, v/v) was passed through the cation

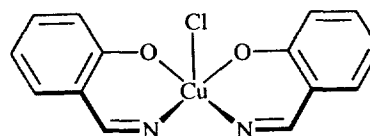
Table 2. O₂ consumption of 3.00 mM of Cu(sal)₂en in CH₂Cl₂

Irradiation time	0.5 hr	1 hr	1.5 hr	2 hr
Immediate detn. after hv	-3.5×10^{-6} M	-0.96×10^{-6} M	2.02×10^{-6} M	3.50×10^{-6} M
14 hr. standing after hv	1.75×10^{-6} M	1.55×10^{-6} M	2.11×10^{-6} M	5.47×10^{-6} M

*O₂ and N₂ partial pressure were 10 mmHg and 737 mmHg for each case.

**Figure 2.** Absorption spectrum of product(1).

exchange resin with increasing ionic strength from 0.01 to 1 N of NaClO₄ and with increasing acidity from 10⁻⁶ M to 10⁻⁴ M of HOAc in 50/50 ethanol-water solution. Although, the attempt mentioned before could not move the red band formed on the top of the column, the anion exchange resin with neutral solvent passed all the isolated product. High valent cationic copper complex formation is suspected. ESR spectrum of product(1) shows the change of Cu(II) compound to Cu(I) or Cu(III) compound⁹ in solid state which is noted by the disappearance of Cu(II) signal. The flash photolysis data shows the presence of short lived species. The short lived species has the maximum absorbance at around 440 nm and the half lifetime 100 μsec in deaerated CH₂Cl₂, 85 μsec in aerated CH₂Cl₂, 300 μsec in 0.01 M acrylamide added CH₂Cl₂. Anti-oxidant acrylamide keeps intermediate stay longer. This indicates that the intermediate is further oxidized to form the final purple product possibly forming Cu(III) and Cl⁻. In many cases, the formation of stable Cu(III) oxo complex is reported¹⁰ in support of proposed structure. The electronic absorption spectrum of the product (1) in ethanol solvent is shown in Figure 2. When comparing the molar absorptivities of Cu(sal)₂en in CH₂Cl₂ and product (1) in ethanol, the absorbance change at 365 nm is mainly due to the loss of Cu(sal)₂en. Irradiation product(1) formed is insoluble in CH₂Cl₂, therefore, the absorption due to product(1) won't effect net absorption spectrum, but the spectral features in ethanol solvent of varying concentration of CH₂Cl₂

**Figure 3.** Proposed structure of product(1), C₁₄H₁₁O₂Cl₂Cu.

showed no detectable increase of absorbance at product(1) absorption peak 544 nm ($\epsilon=7,000$). This implies that the isolated product(1) is secondary reaction product transformed during the isolation process. Moreover, the product(1) is formed only in aerated solvent even though quantum yield for the disappearance of Cu(sal)₂en (Φ -Cu(sal)₂en) is approximately same for both aerated and deaerated solvent. From the all the points mentioned previously, following reaction steps are proposed: (1) Contact or mediation of halogenated solvent to Cu(sal)₂en. (2) Charge transfer from $\sigma_L \rightarrow d$, making ethylene group active to breakage. (3) Electron transfer to form Cl⁻ and cationic copper(III) complex. (4) Secondary reaction with oxygen forming ethylene oxide. After all, structure of product(1) is proposed in Figure 3, where one HCl and 2.5H₂O bound molecules are omitted. Further study of more detailed reaction mechanism is proposed.

Acknowledgment. This work was supported by the Ewha Faculty Research Fund.

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