

# Photochemical study of Tris(2N-salicylidene-5-(O-chloro phenyl)-1,3,4-thiadiazole) iron(III) in different organic solvents

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## Abstract

The photochemistry of chelate complex Tris(2N-salicylidene-5-(O-chloro phenyl)-1,3,4-thiadiazole) iron(III)  $Fe(L)_3$  was studied in five organic solvent: dimethyl sulfoxide (DMSO), methanol (Me), acetone (Ac), ethyl acetate (Ea) and Toluene (To). Monochromatic light of wavelength 365 nm was used for the irradiation process at 25 °C. Uv-visible spectral changes and other observations indicated an intra oxidation-reduction reaction occurring during the photolysis of  $Fe(L)_3$  complex, with homolytic scission of Fe-L bond. The quantum yield ( $\phi_d$ ), rate of photodecomposition and reactivity ratio ( $k_2/k_1$ ) was determined in each solvent. These values always increase as the polarity of the solvent increases and follow the order.

DMSO > Me > Ac > Ea > To

According to the experimental results obtained, the mechanism of photodecomposition of these complexes under the applied conditions was proposed.

## Introduction

The photochemistry of transition metal chelate has been studied extensively during the last decades<sup>(1-5)</sup> with the following main interesting applications:

- 1- Photochemical conversion and storage of solar energy as a photosensitizer in hydrogen production from water splitting, phototoxiation of  $CO_2$  and photogalvanic cell<sup>(6,7)</sup>.
- 2- Photoinitiation of polymerization crosslinking of polymer<sup>(8-9)</sup>.
- 3- Photocatalysts for organic synthesis<sup>(10)</sup>.
- 4- Gasoline octane number improver<sup>(11)</sup>.
- 5- Photostabilization of polymer and photoinducer for polymer degradation<sup>(12)</sup>. The photoredox reaction of  $Fe(acac)_3$  chelate complex was investigated in polystyrene films as photosensitizer degradation<sup>(13)</sup>, (where  $acac = 4,2$  pentanedinate anion).

The photochemical decomposition of Tris[N-(3-ol-1-methyl)butidene (amino) aniline]iron was also studied and the free radical generated was derived from the ligand. It is effectively initiating the photodegradation of polystyrene and poly(methyl methacrylate) films<sup>(14)</sup>. Aliwi and co-workers<sup>(15)</sup> studied  $Fe(III)$  Schiff base chelate complexes for photodegradation of polystyrene. Those authors also observed that the photoredox process had occurred and the free radical responsible in the initiation process was derived from the Schiff base ligand.

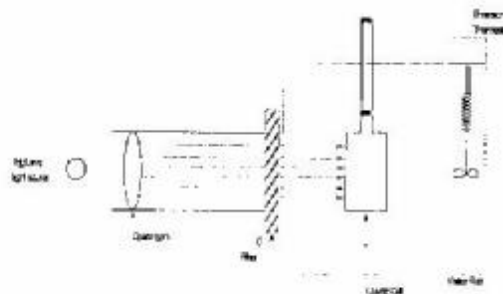
## Materials and Methods

### A. Materials

Tris(2N-salicylidene-5-(O-chloro phenyl)-1,3,4-thiadiazole) iron(III)  $Fe(L)_3$ . This complex was prepared by the method described by Gupta and Pande<sup>(16)</sup>

### B-Techniques

All photolytic experiments were carried out in thermostated quartz cell of 10 mm path length. The photolytic solution were purged by argon gas (purity 99.9%) for 20 minutes before irradiated at 25 °C. A light source, namely high pressure lamp (1000W, Iwasa Ki Electric Co. Ltd, Japan) was used in conjugation with suitable quartz lens and filter (supplied by Kari-Korb C-mb H, Germany) to give essentially a monochromatic beam of wavelength 365 nm. Calibration of filter with the aid of spectrophotometer showed that the transmitted light was predominantly of wavelength 365 nm. The incident light intensity was determined with ferrioxalate actinometer as described by Hatchard and Parker<sup>(17)</sup>. A Perkin-Elmer 1301 uv-visible double beam spectrophotometer was employed to measure the optical densities and the spectral changes during irradiation experiments. Below is a schematic diagram of the used instrument:



## Results and Discussion

### A- Uv-Visible spectrophotometry

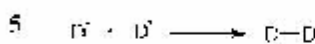
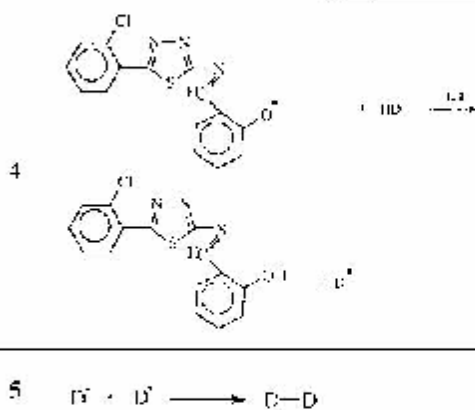
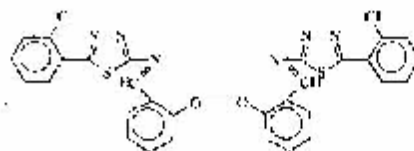
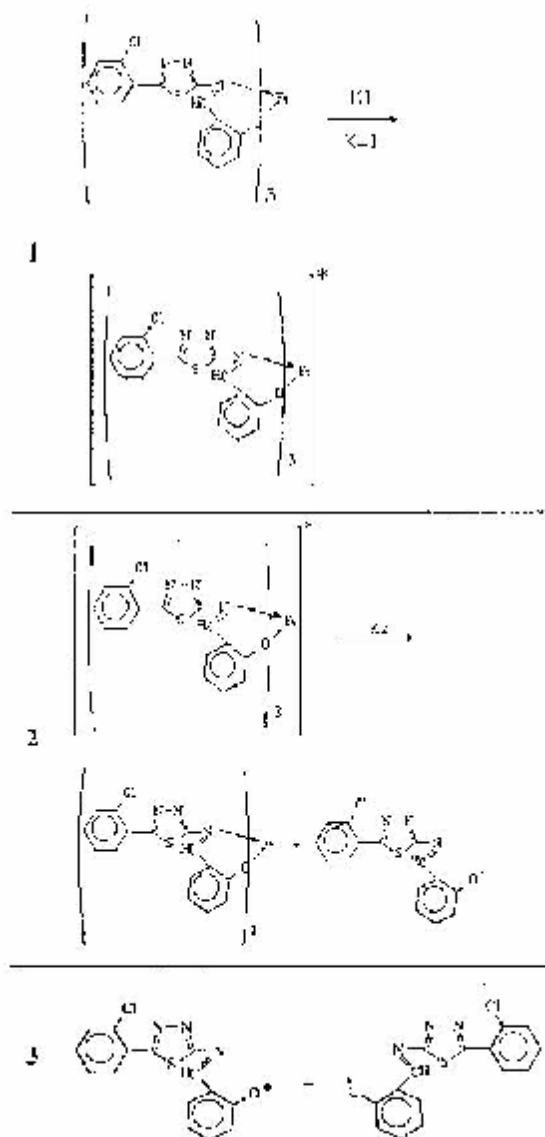
During irradiation time of the chelate complexes in DMSO, Me, Ac, Ea and To at 25 °C, the colour changes gradually from brown to brown-yellow in all solvents. The complexes spectrum changes with

irradiation time, showing a decrease in the absorbance intensity in the visible region between wavelengths 400 to 800

nm., at high concentration of the complex solution; consideration. The absorbance intensity between 200-400 nm. also decreased with irradiation time at lower concentration of the complexes.

### B- Mechanism of the Tris(2N-salicylidene-5-(O-chloro phenyl)-1,3,4-thiadiazole) iron(III) photodecomposition

The uv-visible spectral changes, identification of the photolytic products and other observations. The following mechanism may be suggested for the photodecomposition process (HD = solvent molecule).



The low values of quantum yields of photodecomposition process indicate that the deactivation of the photoexcited chelate ( $FeL3^*$ ) is an important process on this mechanism.

The rate of decomposition

$$= I_{0A_1} \frac{I_{0A_1} k_2}{k_2 + k_1} = \frac{d[FeL_3]}{dt}$$

$$\phi_d = \frac{\text{rate of photodecomposition}}{I_{0A_1}}$$

that

$$k_2 = \frac{\phi_d}{k_1(1 - \phi_d)}$$

### C-The Kinetic Use of UV-Visible Observations

The decay of the  $Fe(L)_3$  complex during irradiation at 365 nm, 25°C in different solvents, has been followed by monitoring the concentration of this complex spectrophotometrically.

From the variation of the concentration of iron complex with time, the rate of photolysis of the complex was deduced. It was found that the change in the concentration varies exponentially with time, which indicates the first order relation of the photoreaction. Therefore from the logarithm plots of the  $A_t - A_\infty$  versus time, the values of the first order specific rate constant ( $k_d$ ) for the complex in different solvents have been determined  $A_t$  is the absorbance of the complex solution at selected wavelength.  $A_\infty$  is the absorbance of the same solution after prolonged irradiation. The variations of  $\ln(A_t - A_\infty)$  with irradiation time of complex. The specific rate constants ( $k_d$ ) for chelate complex were obtained. Table (1) shows the value of light



intensity ( $I_{ph}$ ), the specific rate constant ( $k_d$ ), the quantum yield ( $\phi_d$ ) and reactivity ratio ( $k_2/k_1$ ) of the  $Fe(L)_3$  complex in all solvents used under same conditions.

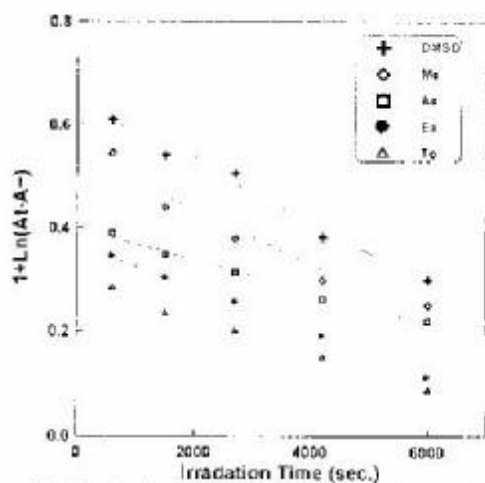
The result shown in Table (1) generally indicates that the  $k_d$  and  $\phi_d$  values are dependent on the type of solvent used. They always increase as the polarity of the solvent increases and follow the order

DMSO > Me > Ac > Ea > To

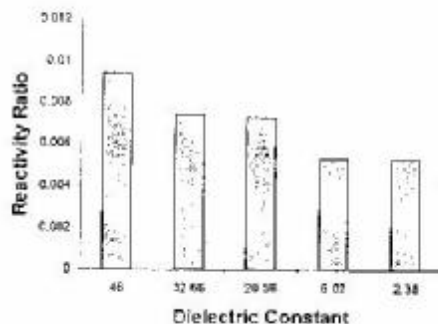
The variation of the values of quantum yield with dielectric constant value of solvent are shown in Figure (1). The results shown in this figure, generally, indicate that  $\phi_d$  increases as the dielectric constant increases; and this might point out to the ionic nature of the excited transition state of the  $Fe(L)_3$  complex in these solvents.

**Table (1) Specific rate constant ( $K_d$ ), the quantum yield ( $\phi_d$ ) and the reactivity ratio ( $K_2/K_1$ ) of the  $Fe(L)_3$  complex in different polar organic solvents (irradiation wavelength 365 nm, at 25 °C).**

Solvent	$10^7$	$10^{-4}$	$10^5$	$10^3$	$10^3$	Dielectric constant
	$I_{ph}$ Ein. $\Gamma^1$ .S $^{-1}$	[Fe(L) $_3$ ] mol / l	$K_d$ sec $^{-1}$	$\phi_d$	$K_2 / K_1$	
DMSO	7.21	1.12	6.47	9.33	9.42	46.45
Me	6.93	1.02	5.55	7.38	7.43	32.66
Ac	7.11	1.14	4.50	7.23	7.28	20.56
Ea	7.83	1.03	4.25	5.28	5.30	6.02
To	6.42	1.12	3.54	5.24	5.27	2.38



**Figure (1) Variation of natural logarithm plot of  $Fe(L)_3$  complex with irradiation time in different organic solvents ( $\lambda_{irr} = 365$  nm, At 25 °C).**



**Figure (2) Variation in reactivity ratio with the dielectric constant of the solvent, for the photodecomposition of  $Fe(L)_3$  complex in different organic solvents.**

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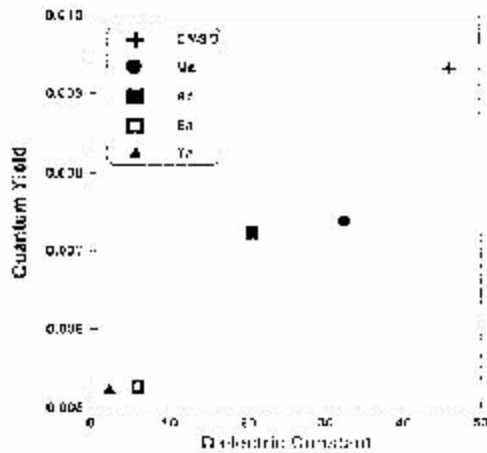
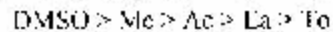


Figure (J) Variation in quantum yields ( $\phi_q$ ) with the dielectric constant of the solvent, for the photodecomposition of  $Fe(L)_3$  complex in different organic solvents.

### إنخلاصة

قد خللنا، نبحث الحالي دراسة كيميائية الضوئية لمعادن الحديد الثلاثي مع الفينولات ثنائي السرة ثلاثي (NO-سلسيليدين-5-اورثر-كلوريد الفينول) (3،5- ثيادايلازول) في خمسة مذيبات عضوية هي: الميثان، ميثانوكسيد، وميثانول، والإيثانول، والـ (Ac)، والإثير، ويتم استخدامه ضوء أحادي ويطلق موجي قدره 365 نانومتر وبدرجة حرارة 25 °C. تلك التغييرات الطيفية الحامسة وملاحظتنا أخرى على حصول تفاعل أكسدة-الازرق، الذي خلال عملية تفاعل التحوّل للمعدن  $Fe(L)_3$  مع استخدام مقياس الأشعة UV-Vis.

لقد تم حساب الكفاءة الناتجة ( $\phi_q$ )، ودرجة التفكك الضوئي ودرجة الكمية ( $k_d/k_f$ ) في كل مذيب من المذيبات اعلاه ووجد ان هذه القيم تزداد بزيادة قطبية المذيب، ووفق الترتيب الآتي:



ولمبدأ النتائج العملية المستحصلة، تم اقتراح ميكانيكية التفاعل الضوئي لهذه المعقدات تحت الظروف المختبرية المذكورة سابقاً.