

PHOTOCHEMICAL STUDY OF TRIS(ETHYLXANTHATO) IRON(III) IN DIFFERENT ORGANIC SOLVENTS

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Abstract

The photochemistry of Tris(ethylxanthato) iron(III) was studied in five organic solvents: dimethyl sulfoxide (DMSO), methanol, acetone, ethyl acetate and Benzene. 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(etc)₃ complex, with homolytic scission of Fe-S bond. The quantum yield (ϕ_d), rate of photodecomposition and reactivity ratio (k_2/k_{-1}) were determined in each solvent. These values always increase as the polarity of the solvent increased and following the order.

DMSO > Methanol > Acetone > Ethyl acetate > Benzene

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⁽¹⁻⁵⁾ 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 CO₂ and photo galvanic cell^(6,7).
- 2- Photoinitiation of polymerization cross-linking of polymers⁽⁸⁻⁹⁾.
- 3- Photocatalysts for organic synthesis⁽¹⁰⁾.
- 4- Gasoline octane number improvers⁽¹¹⁾.
- 5- Photostabilization of polymer and photo-inducer for polymer degradation⁽¹²⁾. The redox reaction of Fe (acac)₃ chelate complex was investigated in polystyrene films as photosensitizer degradation⁽¹³⁾, (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⁽¹⁴⁾. Aliwi and et al.⁽¹⁵⁾ reported the use of Fe(III) Schiff base chelate complexes for photodegradation of polystyrene. They for also observed that the photoredox process had

occurred and the free radical responsible the initiation process was derived from the Schiff base ligand.

Materials and Methods

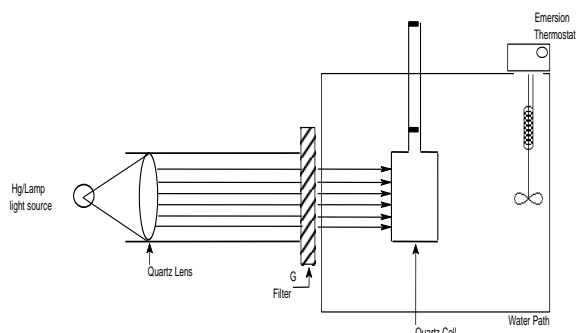
A. Materials

Tris(ethylxanthato) iron (III), This complex was prepared according the method reporting in literature.⁽¹⁶⁾

B-Techniques

All photolytic experiments were carried out in thermostated quartz cell of 10 mm path length. The photolytic solution was 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⁽¹⁷⁾. A Perkin-Elmer 1301 Uv-Vis. 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 spectrophotometr*

During irradiation time of chelate complexes the in dimethyl sulfoxide (DMSO), methanol, acetone, ethyl acetate and Benzene at 25 °C, the colour was 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. The absorbance intensity between 200-400 nm. also decreased with irradiation time at lower concentration of the complexes.

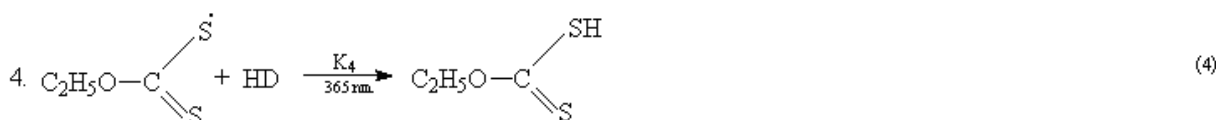
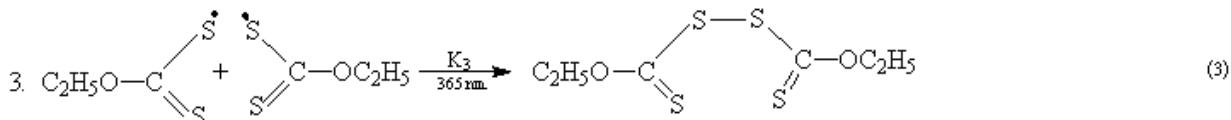
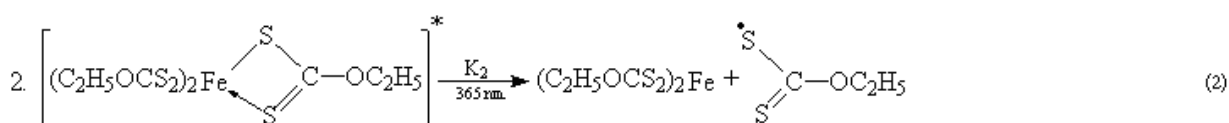
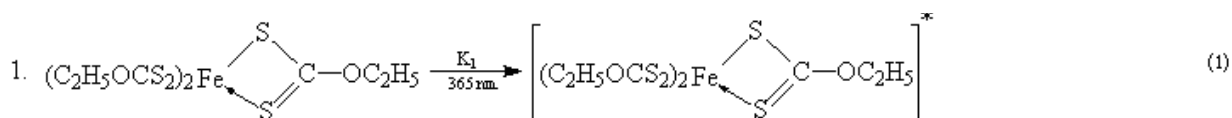
B- *Identification of the photolytic products*

Identification methods are adopted to identify the photolytic products. Solution of $\text{Fe}(\text{etx})_3$ in benzene free from carbon disulfide, was irradiated for about 50 hours at $\lambda_{\text{irr}} = 365$ nm. (at 25 °C). The complex fragmented to $(\text{C}_2\text{H}_5\text{OCS}_2)_2\text{Fe}(\text{II})$ and xanthate radical as the first step of the decomposition as shown in equations (2).

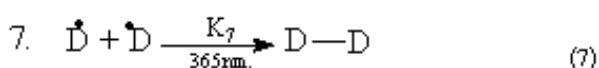
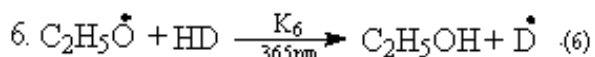
Xanthate radical combines with the same radical as shown in equation (3), a positive test obtained for S-S bond, which indicated the formation of the compound to expect this compound formed.

Xanthate radical abstract hydrogen atom from solvent molecule as shown in equation below a positive test obtained for S-H bond, which indicated the formation of the expect xanthic acid equation (4).

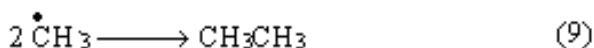
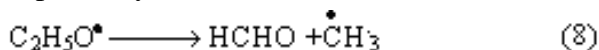
Also, xanthate radical fragmented to carbon disulfide and ethoxy radical as shown in equation (5).



To ensure that CS₂ was liberated in this photolytic reaction, CS₂ analysis was carried out⁽¹⁹⁾ and a positive test obtained. The same result was got upon irradiation of a solution of Fe(etx)₃ complex in acetone solvent. Ethoxy radical obtained from the second step of decomposition of the complex abstracted a hydrogen atom from the solvent molecule (HD) and produced ethanol⁽²⁰⁾. The radical derived from the solvent D[•] could combine to form a dimer of solvent molecules (D-D) as shown in equations (6) and (7) respectively:



Ethoxy radical C₂H₅O[•] may be oxidize to aldehyde as shown in equations (8) and (9) respectively:



However, the test for formaldehyde was negative⁽¹⁸⁾. Apparently, the oxidation processes may stop after the ethoxy radical had abstracted hydrogen from the solvent.

Accordingly, one would expect that an intra oxidation-reduction reaction occurs during the photolysis of Fe(etx)₃ complex, with homolytic scission of Fe-S bond to form radical fragments as explained above.

C- Mechanism of the tris(ethylxanthato) iron(III) photodecomposition

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

$$\text{The rate of decomposition} = I_{\text{abs}} \frac{I_{\text{abs}} k_{-1}}{k_{-1} + k_2} - \frac{d[\text{FeL}_3]}{dt} = \dots\dots\dots(1)$$

$$\phi_d = \frac{\text{rate of photodecomposition}}{I_{\text{abs}}} \dots\dots\dots(2)$$

Then

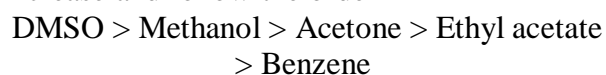
$$\frac{k_2}{k_{-1}} = \frac{\phi_d}{1 - \phi_d} \dots\dots\dots(3)$$

D-The Kinetic Use of Uv-Visible Observations

The decay of the Fe(etx)₃ complex during irradiation at 365 nm. And 25 °C in different solvents, has been followed by monitoring the concentration of this complex spectrophotometrically.

From the variation of the concentration of iron(III) 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_∞ versus time, the values of the first order specific rate constant (k_d) for the complex in different solvents was determined, where A_t is the absorbance of the complex solution at selected wavelength, A_∞ is the absorbance of the same solution after prolonged irradiation. The variations of ln(A_t-A_∞) with irradiation time (t) of complex. The specific rate constants (k_d) for chelate complex were obtained. Table (1) shows the values of light intensity (I_{ab}), the specific rate constant (k_d), the quantum yield (φ_d) and reactivity ratio (k₂/k₋₁) of the Fe(etx)₃ complex in all solvents used under the same conditions.

The result shown in Table (1) generally indicate that the k_d and φ_d values are dependent on the type of solvent used. They always increase as the polarity of the solvents increase and follow the order



The variation of the values of quantum yield with dielectric constant value of solvent are shown in Fig. (1). These results in this, generally, indicate that φ_d increases as the dielectric constant increases; and this might point out the ionic nature of the excited transition state of the Fe(etx)₃ complex in these solvents.

Table (1)

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

Solvent	$10^{-7} I_{abs}$ $Ein.l^{-1}.S^{-1}$	10^{-4} [Fe(etx) ₃] mol / l	10^{-5} K_d Sec ⁻¹	$10^{-3} \phi_d$	10^{-3} K_2 / K_1	Dielectric constant
DMSO	7.32	1.21	5.78	4.78	9.22	46.45
Methanol	7.21	1.23	5.34	4.34	7.71	32.66
Acetone	7.51	1.22	5.01	4.11	7.04	20.56
Ethyl acetate	6.53	1.29	4.18	5.28	4.48	6.02
Benzene	7.22	1.18	3.22	2.73	3.73	2.27

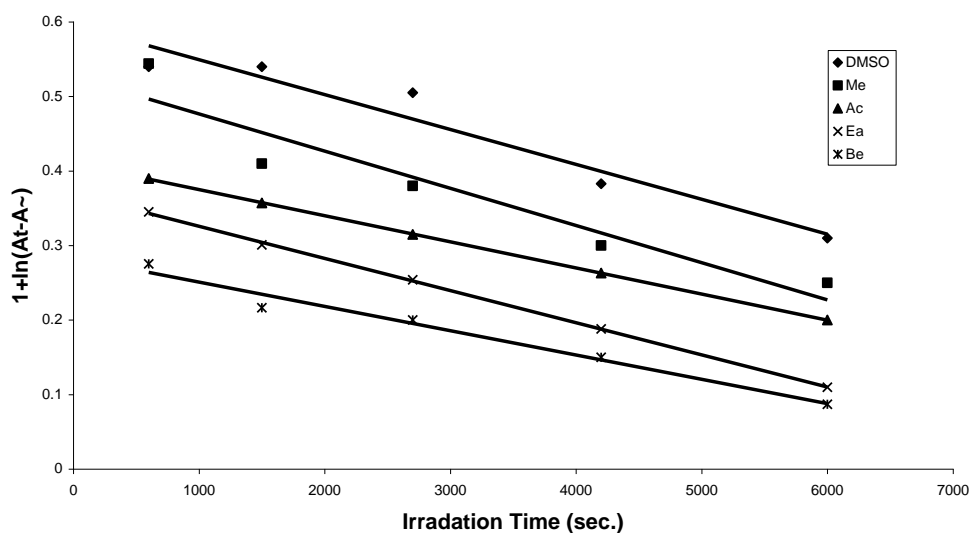


Fig.(1) : Variation of natural logarithm plot of $Fe(etx)_3$ complex with irradiation time in different organic solvents ($\lambda_{irr.} = 365$ nm. At 25 °C).

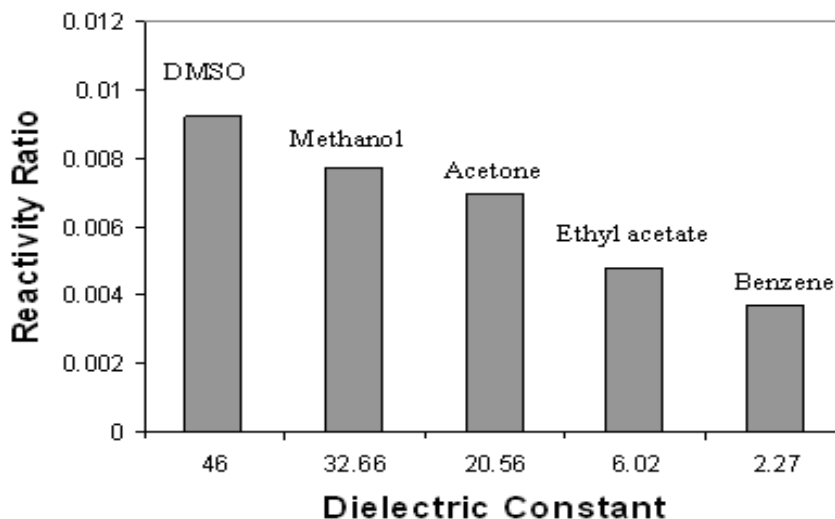


Fig.(2) : Variation in reactivity ratio with the dielectric constant of the solvent, for the photodecomposition of $Fe(etx)_3$ complex in different organic solvents.

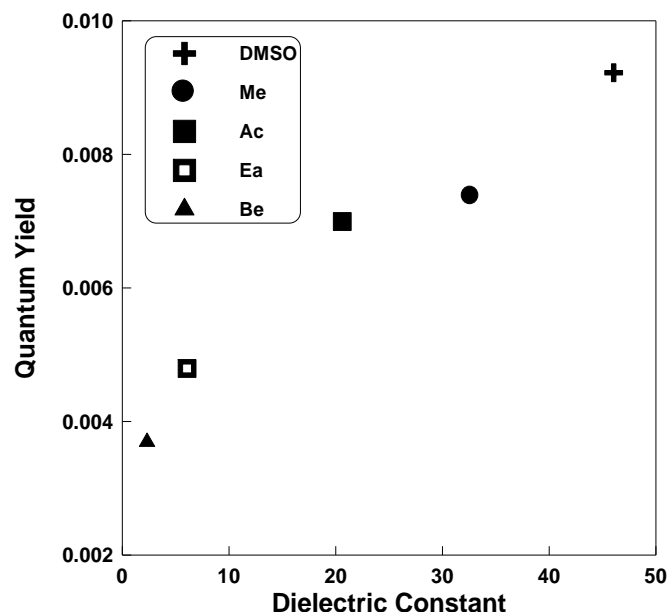


Fig.(3) : Variation in quantum yields (ϕ_d) with the dielectric constant of the solvent, for the photodecomposition of $Fe(etc)_3$ complex in different organic solvents.

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الخلاصة

تم خلال البحث الحالي دراسة الكيمياء الضوئية لمعقدات الحديد الثلاثي مع الليكاند ثنائي السن : ثلاثي (أثيل زانثيت) في خمسة مذيبات عضوية هي: ثنائي الميثيل سلفواوكسايد والميثانول والأسيتون واسيتات الاثيل والبنزين. وتم استخدام ضوء أحادي وبطول موجي قدره 365 نانوميتر وبدرجة حرارة 25°. لقد دلت التغييرات الطيفية الحاصلة للمعقد وملاحظات أخرى على حصول

تفاعل من نوع أكسدة-اختزال داخلي خلال عملية التفاعل
الضوئي للمعدن $Fe(etx)_3$ مع انفصام متجانس للأصرة
. Fe-S

لقد تم حساب المنتج الكمي (ϕ_d) وسرعة التفكك
الضوئي ونسبة الفعالية (k_2/k_1) في كل مذيب من المذيبات
المستخدمة ووجد ان هذه القيم تزداد بزيادة قطبية المذيب
ووفق الترتيب الآتي :

DMSO > Methanol > Acetone > Ethyl acetate > Benzene

وطبقاً للنتائج العملية المستحصلة ، تم اقتراح ميكانيكية
التفكك الضوئي لهذه المعقدات تحت الظروف المختبرية
المذكورة سابقاً.