Photochemical Study of 2-(6-Methoxynaphthalen-2-yl) Propanoic Acid Iron(III) in Different Organic Solvents

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Abstract

The photochemistry of chelate complex 2-(6-methoxynaphthalen-2-yl) propanoic acid iron (III) $Fe(L)_3$ was studied in three polar aprotic solvents: Dimethyl sulfoxide (DMSO), Dimethyl form amide (DMF), Acetone (Ac). Monochromatic light of wavelength 311 nm was utilized for the irradiation-process at 25^{o}C. UV-VIS changes demonstrated an intraoxidation-reduction response happening amid the photolysis of $Fe(L)_3$ complex, with homolytic scission of Fe-L bond. Quantum yield (Q_d), rate of photodecomposition and reactivity proportion (k_2/k_{-1}) was resolved in every used solvent. These values dependably increment as polarity of the solvent increments and take after the order: DMSO > DMF > Ac. The mechanism of photodecomposition of this complex under the connected conditions was proposed.

Keywords: Photochemistry; Iron(III); Dimethyl sulfoxide; Dimethyl form amid; acetone

دراسة الكيمياء الضوئية لمعقد الحديد الثلاثي مع الليكاند ثنائي السن
2-(6-methoxynapthalen-2-yl) propanoic acid
في مذيبات عضوية مختلفة

الخلاصة

درست الكيمياء الضوئية لـ (معقد الحديد الثلاثي مع الليكاند ثنائي السن) (2-(6-methoxynaphthalen-2-yl) propanoic acid) في ثلاث مذيبات عضوية هي (ثنائي المثيل سلفواوكسايد وثنائي مثيل فورمامايد والأسيتون). وقد استخدم ضوء أحادي وبطول موجي قدره 311 نانوميتر وبدرجة حرارة 25^{o}م. لقد دلت التغيرات الطيفية الحاصلة وملاحظات أخرى على حصول

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تفاعل أكسدة-اختزال ضمني خلال عملية التفاعل الضوئي للمعقد $(Fe(L)_3)$ مع انفصام متجانس للآصرة (Fe-L). لقد تم حساب الناتج الكمي (Q_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 > DMF > Ac** وفقا للنتائج العملية المستحصلة، تم اقتراح ميكانيكية التفكك الضوئي لمعقد الحديد الثلاثي.

الكلمات المرشدة: الكيمياء الضوئية، الحديد الثلاثي، ثنائي مثيل سلفوكسايد، ثنائي مثيل فورامايد، الاسيتون

INTRODUCTION

Photochemistry, the branch of science that arrangements with the compound procedures that are brought on by the assimilation of light vitality. The procedure by which a photochemical response is done is called photolysis. Photolysis is normally started by infrared, obvious, or bright light [1-2]. The photochemistry of move metal edifices [3] has been concentrated broadly [4-5], not just as a result of their wide application in regions, for example, substance actinometry [6], radical polymerization response start [7], corruption of natural poisons [8] and as sunlight based vitality media [9], additionally in light of the fact that they have served as course book models for electron exchange (ET) [10-11] and stereochemistry [12]. For a long stretch, move metal trisoxalato buildings were thought to experience solely intramolecular ET, instantly after light inside the charge-exchange band. This theory depended on ceaseless wave, streak photolysis [13-16] and nanosecond laser spectroscopic exploratory results [17]. In both watery and nonaqueous arrangements [18-19]. Intermolecular light-actuated electron exchange including move metal edifices has been broadly considered amid the most recent 15 years [20]. This interest was fortified, in any event somewhat, by endeavors to build up a counterfeit photosynthesis for the change and substance stockpiling of sunlight based vitality [21]. It is understood that characteristic photosynthesis requires a light-impelled electron exchange as the fundamental procedure.

Intermolecular photochemical electron exchange happens by two unique instruments. Initial, an electronically energized particle may experience an electron trade with another atom in its ground state. In addition, a direct optical electron exchange can be accomplished if the electron benefactor and acceptor are electronically coupled by a nearby contact. Aprotic solvents are polar; they do not act as Bronsted acids towards water. Polar aprotic solvents give a polar response environment and are as often as possible utilized for SN2 relocation responses, where they settle the charge-detachment that happens in the move state. They are hydrogen-bond acceptors, however not hydrogen bond contributors. In this work, we provide details regarding the photochemical impacts of the arrangement of aprotic solvents (Acetone, DMF, and DMSO) on the chelate complex of one of move metals.

Experimental

Materials

The 2-(6-methoxynaphthalen-2-yl) propanoic acid Iron (III) $Fe(L)_3$ complex was prepared by the method described by [22].

Techniques

All photolytic tests were completed in thermostated quartz cell of 10 mm path length. The photolytic arrangement were cleansed by argon gas (virtue 99.9 %) for 20 minutes before illuminated at 25oC. A light source, to be specific high weight light (1000 W. lwasa Ki Electric Co. Ltd., Japan) was utilized as a part of conjugation with appropriate quartz lens and channel (supplied by Karl-Korb, GmbH, Germany) to give basically a monochromatic light emission 311 nm Calibration of channel with the guide of spectrophotometer demonstrated that the transmitted light was transcendently of wavelength 311 nm. The occurrence light power was resolved with ferrioxalate actinometer as portrayed by Hatchard and Parker [23]. A Perkin–Elmer 1301 UV-VIS twofold shaft spectrophotometer was utilized to measure the optical densities and the phantom changes amid illumination tests. Figure 1 demonstrates the schematic chart of the utilized instrument.

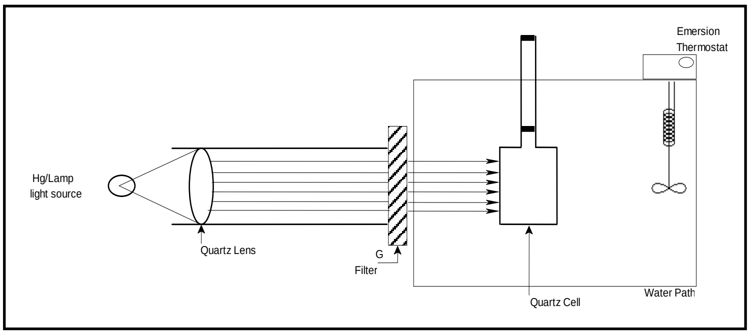


Figure (1). Schematic diagram of the used instrument

Results and Discussion

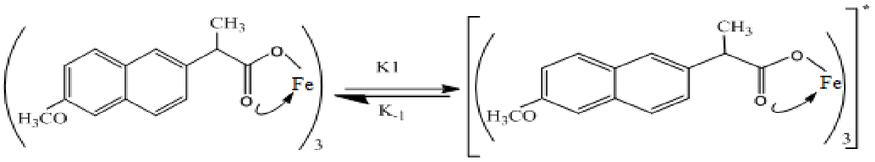
UV-visible spectrophotometer

Amid illumination time of the Fe(III) complex in DMSO, DMF and Ac, at 25^{o}C, the shading changes progressively from yellow to light yellow in all solvents. The intricate range changes with light time, demonstrating a lessening in the absorbance force between (200-400) nm with illumination time at lower convergence of the buildings.

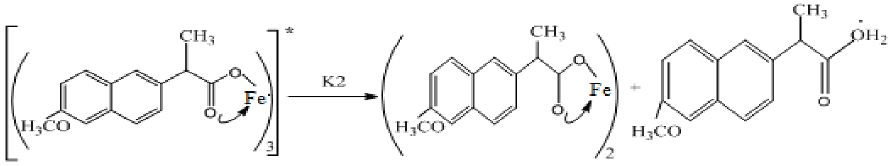
The absorbance force in the obvious locale between wavelengths (400-800) nm, also diminished with illumination time, at high convergence of the overwhelming arrangement thought.

Mechanism of the 2-(6-methoxynaphthalen-2-yl) propanoic acid iron (III) photodecomposition

The UV-Visible spectral changes, identification of the photolytic items and different perceptions. The accompanying instrument might be proposed for the photodecomposition process (HD = dissolvable particle).



(1)



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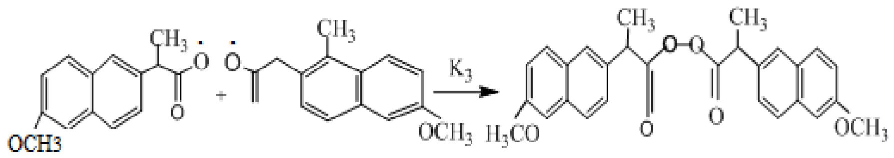

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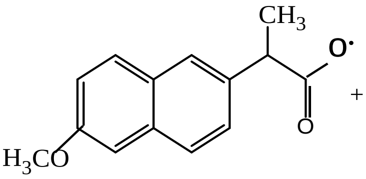

$+$ solvent molecule $\xrightarrow{K_4}$ product (4)

The low values of quantum yields of Photodecomposition process indicate that the deactivation of the photoexcited chelate (K_{-1}) is an important process on this mechanism.

$$\text{The rate of decomposition} = I_{Abs} - \frac{I_{Abs}K_{-1}}{K_{-1}+K_2} - \frac{d[FeL_3]}{dt} \qquad (5)$$

$$Q_d = \frac{\text{rate of photodecomposition}}{I_{Abs}} \qquad (6)$$

than

$$\frac{K_2}{K_{-1}} = \frac{Q_d}{1-Q_d} \qquad (7)$$

The kinetic use of UV-visible observations

Decay of the Fe(L)$_3$ complex amid illumination at 311 nm 25^{o}C in various solvents, had been trailed by checking the grouping of this complex spectrophototometrically.

From the logarithm-plots of the A_t-A_∞ vs time, the estimations of the 1st-order particular rate steady (k_d) for the complex in various solvents have been resolved At is the absorbance of the unpredictable arrangement at chose wavelength. A_∞ is the absorbance of the same arrangement after delayed illumination. The varieties of ln(A_t-A_∞) with illumination time (t) of complex. The particular rate constants (k_d) for Fe(III) complex were gotten [24].

Table 1 demonstrates the estimation of light force (I_{abs}), the particular rate consistent (k_d), the quantum yield (Q_d) and reactivity proportion (K_2/K_{-1}) of the Fe(III) complex in all solvents utilized under same conditions.

The outcome appeared in Table 1 by and large demonstrates that the kd and Qd qualities are reliant on the kind of dissolvable utilized. They generally increment as the extremity of the dissolvable increments and take after the request:

DMSO > DMF > Ac

The variety of the estimations of quantum yield with dielectric steady estimation of dissolvable are appeared in Figure 2. The outcomes appeared in this Figure, for the most part, demonstrate that Q_d increments as the dielectric consistent expansions; and this may call attention to the ionic way of the energized move condition of the Fe(III) complex in these solvents. Moreover, Figure 3 explains the Variety of reactivity ratio with the dielectric constant of the solvent for the Photodecomposition of Fe(L)$_3$ complex in different polar aprotic solvents, and variation of natural logarithm plot of Fe(L)$_3$ complex with irradiation time in different organic solvents (λirr. = 311 nm at 25 ^{O}C) shows in Figures 4 and Table 2.

Table (1). Rate constant K_d, the quantum yield Q_d and the reactivity ratio K_2/K_{-1} of the Fe(L)$_3$ (1×10^{-5} mol/l) complex in different polar aprotic organic solvents

Solvent	Dielectric Constant	10^{-5} k_d (sec^{-1})	10^{-10} Q_d	10^{-10} K_2 / K_{-1}
DMSO	46.7	0.010	3. 1	3.431
DMF	38	0.022	2.04	2.038
Ac	21	0.014	1.430	1.009

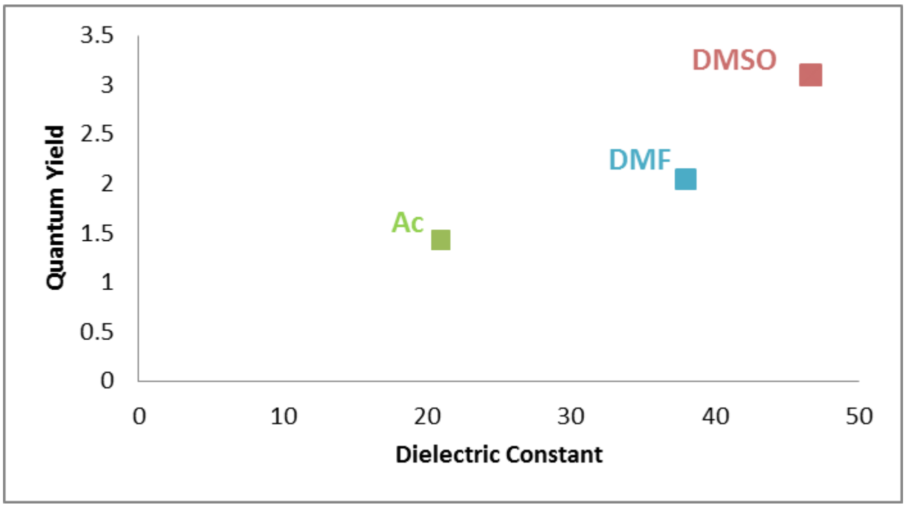

Figure (2). Variation in quantum yields Q_d with the dielectric constant of the solvent, for the photodecomposition of $Fe(L)_3$ complex in different polar aprotic solvents

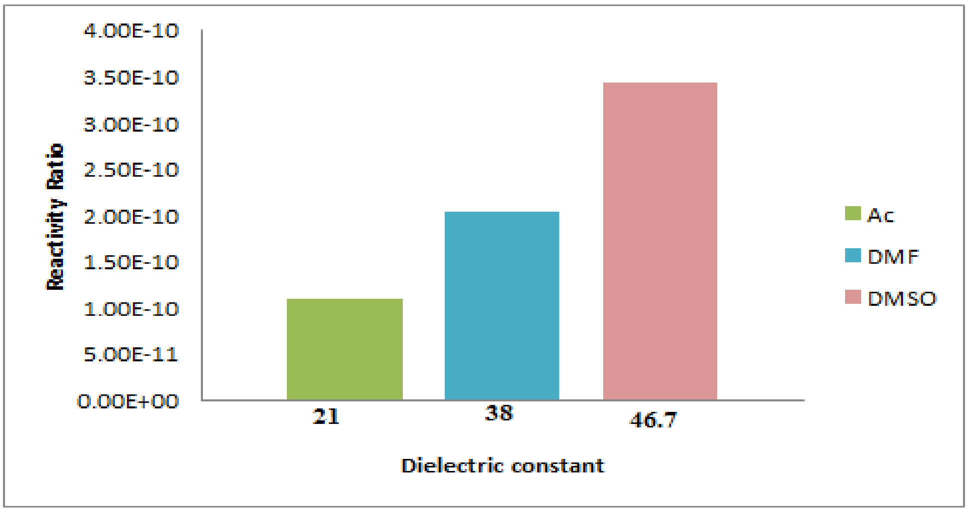

Figure (3). Variation in reactivity ratio with the dielectric constant of the solvent, for the Photodecomposition of $Fe(L)_3$ complex in different polar aprotic solvents

Table (2). Variation of natural logarithm plot of $Fe(L)_3$ complex with irradiation time in different organic solvents ($\lambda_{irr.}$ = 311 nm at $25^{\circ}C$).

Irradiation Time	Solvents		
	DMSO	DMF	Ac
0	3.133	2.113	1.76
15	2.9	2.05	1.5
30	2.614	1.976	1.234
45	2.51	1.801	0.92
60	2.1	1.4	0.8

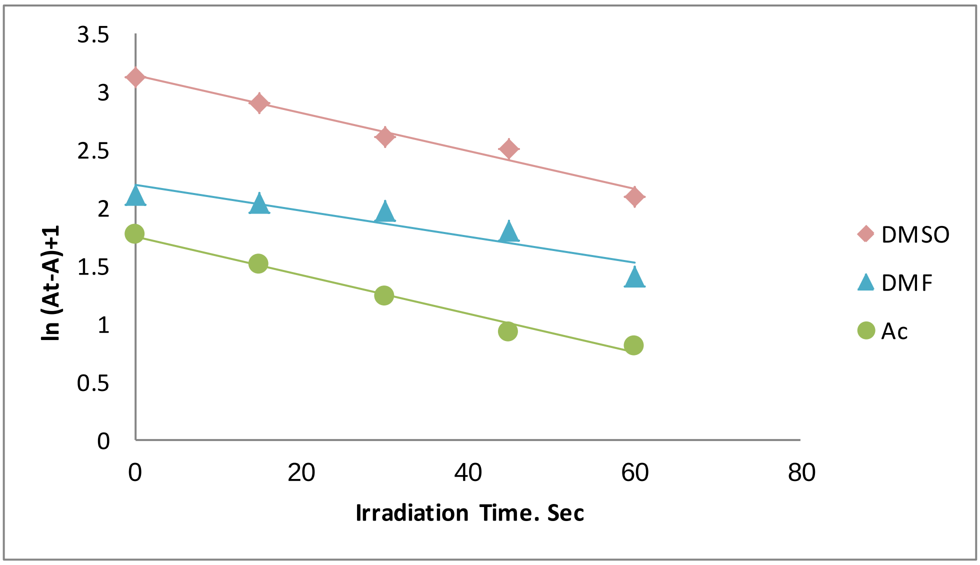

Figure (4). Variation of natural logarithm plot of $Fe(L)_3$ complex with irradiation time in different organic solvents ($\lambda_{irr.}$ = 311 nm at 25 ^{0}C).

Conclusion

In this work, the photochemical of chelate complex 2-(6-methoxynaphthalen-2-yl)propanoic corrosive Iron (III) $Fe(L)_3$ was studied in three polar aprotic solvents: dimethyl sulfoxide (DMSO), dimethylformamide (DMF), $(CH3)_2CO$ (Ac) were concentrated on The quantum yield (Q_d), rate of photodecomption and reactivity

proportion (K_2/K_{-1}) was resolved in every dissolvable. These qualities dependably increment as the extremity of the dissolvable increments and take after the request:
DMSO > DMF > Ac

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