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

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Abstract

The photochemistry of chelate complex 2-(6-methoxynaphthalen-2-yl)propanoic acid chromium (III) $Cr(L)_3$ was studied in three polar aprotic solvents: Dimethyl sulfoxide (DMSO), Dimethylformamide (DMF), Acetone (Ac). Monochromatic light of wavelength 311 nm was used for the irradiation processes at 25 ^oC. Uv-visible spectral changes indicates an intra oxidation-reduction reaction occuring during the photolysis of $Cr(L)_3$ complex, with homolytic scission of Cr-L bond. The quantum yield (ϕ_d), rate of photodecomption and reactivity ratio (k_2/k_{-1}) were determined in each solvent. These values always increase as the polarity of the solvent increases and follow the order: DMSO > DMF > AC **.** Mechanism of photodecomposition of this complex under the applied conditions was proposed.

دراسة الكيمياء الضوئية لـمعقد الكروم 2-(6-methoxynaphthalen-2-yl)Propanoic Acid الثلاثي مع
في مذيبات عضوية مختلفة

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الخلاصة

تم دراسة الكيمياء الضوئية لمعقد الكروم الثلاثي مع الليكاند ثنائي السن: 2-(6-methoxynaphthalen-2-yl)propanoic acid في ثلاث مذيبات قطبية لا بروتونية هي: ثنائي مثيل سلفواوكسايد وثنائي مثيل فورامايد والأسيتون. وتم استخدام ضوء أحادي وبطول موجي قدره ٣١١ نانوميتر وبدرجة حرارة ٢٥°. لقد دلت التغيرات الطيفية الحاصلة وملاحظات أخرى على حصول تفاعل أكسدة-اختزال داخلي خلال عملية التفاعل الضوئي للمعقد $Cr(L)_3$ مع انفصام متجانس للآصرة Cr-L. لقد تم حساب الناتج الكمي (Q_d) وسرعة التفكك الضوئي ونسبة الفعالية (K_2/K_{-1}) في كل مذيب من المذيبات أعلاه ووجد ان هذه القيم تزداد بزيادة قطبية المذيب ووفق الترتيب الآتي:

DMSO > DMF > AC

ووفقا للنتائج العملية المستحصلة، تم أقتراح ميكانيكية التفكك الضوئي لمعقد الكروم الثلاثي.

Keywords: Photochemistry, Spectroscopy, Chromium(III), Solvents

Introduction

Photochemistry is the branch of chemistry that is concerned with the chemical effects of light. Generally, this term is used to describe a chemical reaction caused by absorption of ultraviolet (wavelength from 200 to 400 nm), visible light (400-750 nm) or infrared radiation (750-2500 nm). The exchange of an electron between two molecules may be considered to be the most fundamental and important chemical reaction. Such a redox process can occur thermally or photochemically. Intermolecular light-induced electron transfer involving transition metal complexes has been extensively studied during the last 15 years [1,2].

The photochemistry of transition metal chelate has 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 photoglvanic cell [3,4].
2. Photointation of polymerization crosslinking of polymer .
3. Photostabilization of polymer and photoinducer for polymer degradation [5].

The photophysical and photochemical properties of metal-free and zinc (II) phthalocyanine compounds have been studied in DMF and toluene in order to investigate of polar and non-polar solvent effect on these properties [6]. The photophysics of a new class of styryl dyes has been studied in organic media, the ground and excited state dipole moments have been determined. The dye forms a dye–solvent complex in dichloromethane [7] the photostability of avobenzone(4-tert-butyl-4-methoxydibenzoylmethane) in four solvents were investigated. Avobenzone was found to be photostable in methanol but not in DMSO, ethyl acetate or cyclohexane. UV, GC–MS, HPLC and NMR studies showed that avobenzone predominantly photoisomerises in DMSO but principally photodegrades n cyclohexane, whereas both processes occur in ethyl acetate [8]. The prolificacy of the photophysical and photochemical properties of diimine rhenium(I) tricarbonyl complexes allows for a range of important applications such as lightemitting devices, sensors, probes for photo-polymerization, optical switches, nonlinear optical materials, radiopharmaceuticals, carbon dioxide reduction and supramolecular chemistry. Novel photoresponsive chelators Oxa-ester and Oxa for divalent cations were designed and synthesized [9].

Experimental Part

A. Materials

The 2-(6-methoxynaphthalen-2-yl)propanoic acid chromium (III) $Cr(L)_3$ complex was prepared by the method that was described by Ibrahim *et al*. [10].

B. Techniques

All photolytic experiments were carried out in thermostated quartz cell of 10 mm pathlength, the photolytic solution was purged with argon gas (purity 99.9%) for 20 minutes before irradiation at 25 ^{o}C. A light source, namely high pressure lamp (1000 W. l wasa 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 311 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 [12]. A Perkin–Elmer 1301 Uv-visible doble beam spectrophotometer was employed to measure the optical densities and the spectral changes during irradiation experiments. Figure (1) shows the schematic diagram of the used instrument:

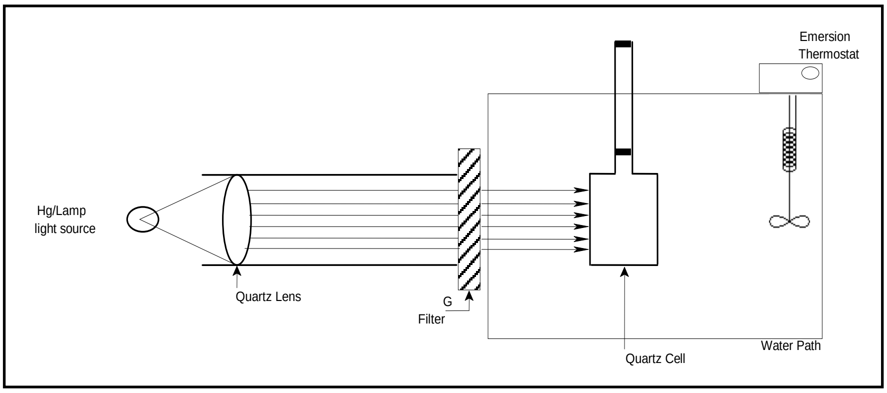


Figure (1): Schematic diagram of the used photoreactor unit.

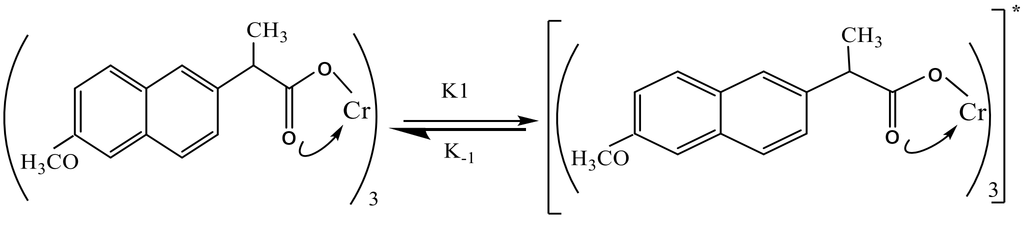
Results and Discussion

A. UV-Visible spectrophotometer

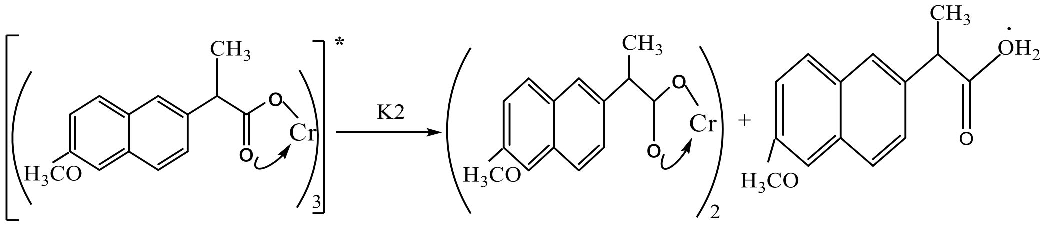
During irradiation time of the Cr(III) complex in DMSO, DMF and Ac, at 25^{o}C, the colour changes gradually from green to light green in all solvents. The changes in complex spectrum with irradiation time, shows a decrease in the absorbance intensity in the visible region between wavelengths (400-800) nm, at high concentration of the complex solution consideration. The absorbance intensity between (200-400) nm was decreased with irradiation time at lower concentration of the complexes.

B. Mechanism of the 2-(6-methoxynaphthalen-2-yl)propanoic acid chromium (III) photodecomposition

The UV-Visible spectral changes are related to the photolytic products and other species that are produced upon. The following mechanism (Eq. (1-8)) may be suggested for the photodecomposition process.



(1)



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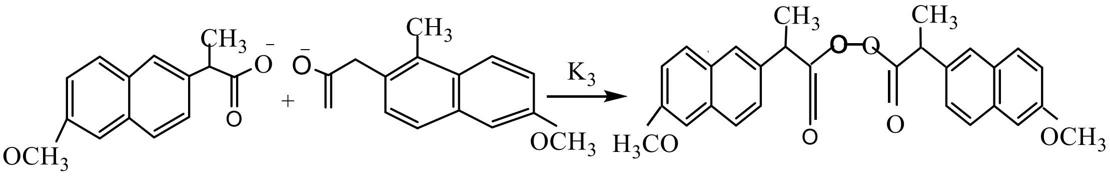
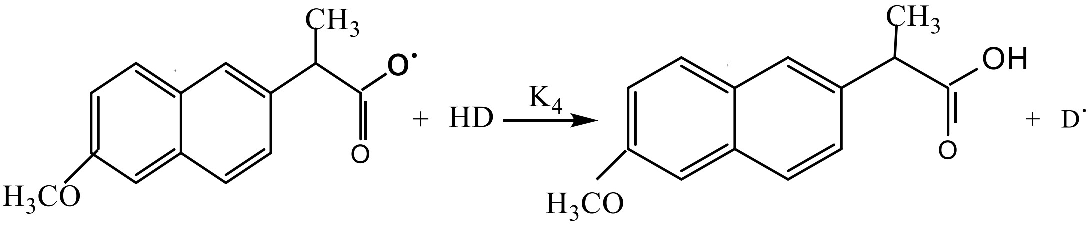


(3)



(4)

$$D^{\bullet} + D^{\bullet} \xrightarrow{K_5} D - D \qquad (5)$$

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.

$$\text{The rate of decomposition} = I_{Abs} - \frac{I_{Abs}K_{-1}}{K_{-1}+K_{2}} - \frac{d\left[CrL_{3}\right]}{dt} \qquad (6)$$

$$Q_d = \frac{\text{rate of photodecomposition}}{I_{Abs}} \qquad (7)$$

than

$$\frac{K_2}{K_{-1}} = \frac{Q_d}{1-Q_d} \qquad (8)$$

C. Kinetic use of the UV-Visible

The decay of the $Cr(L)_3$ complex during irradiation at 311 nm 25 ^oC in different solvents, has been followed by monitoring the concentration of this complex spectrophototometrically. 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 have been determined 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 $\ln(A_t-A_\infty)$ with irradiation time (t) of complex. The specific rate constants (k_d) for Cr(III) complex were obtained. Table (1) shows the value of light intensity (I_{Abs}), the specific rate constant (k_d), the quantum yield (Q_d) and reactivity ratio (K_2/K_{-1}) of the Cr(III) complex in all solvents used under same conditions.

The results shown in Table (1) generally indicates that the k_d and Q_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 > DMF > AC

The variation of the values of quantum yield with dielectric constant values of solvents are shown in Figure (2). These results are shown in this Figure. Generally, indicate that Q_d increases as the dielectric constant increases; and this might point out to the ionic nature of the excited transition state of the Cr(III) complex in these solvents.

Table (1): Rate constant (k_d), the quantum yield (Q_d) and the reactivity ratio (K_2/K_{-1}) of the $Cr(L)_3$ (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	1.430	3.431
DMF	38	0.014	2.039	2.038
AC	21	0.022	3.094	1.099

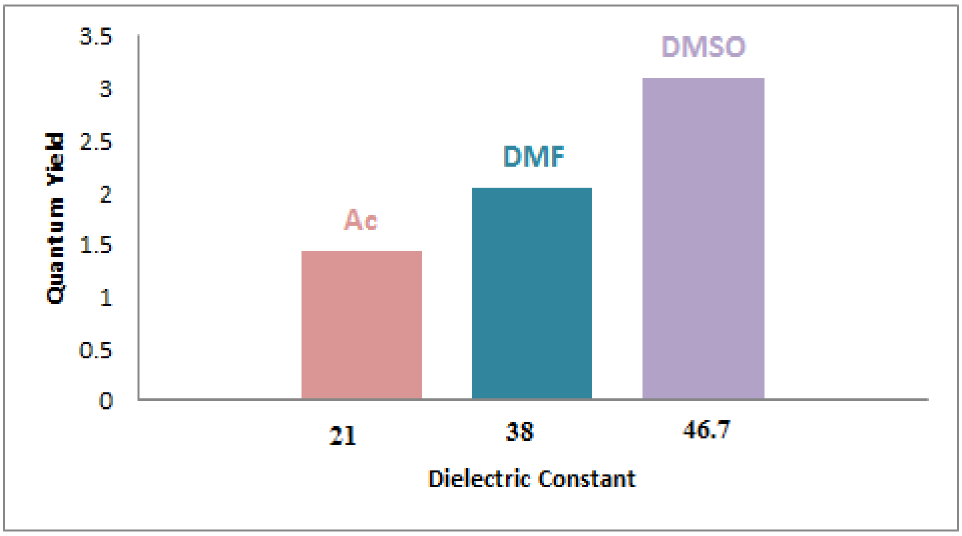


Figure (2): Variation in quantum yields (Q_d) with the dielectric constant of the solvent, for the photodecomposition of $Cr(L)_3$ complex in different polar aprotic solvents.

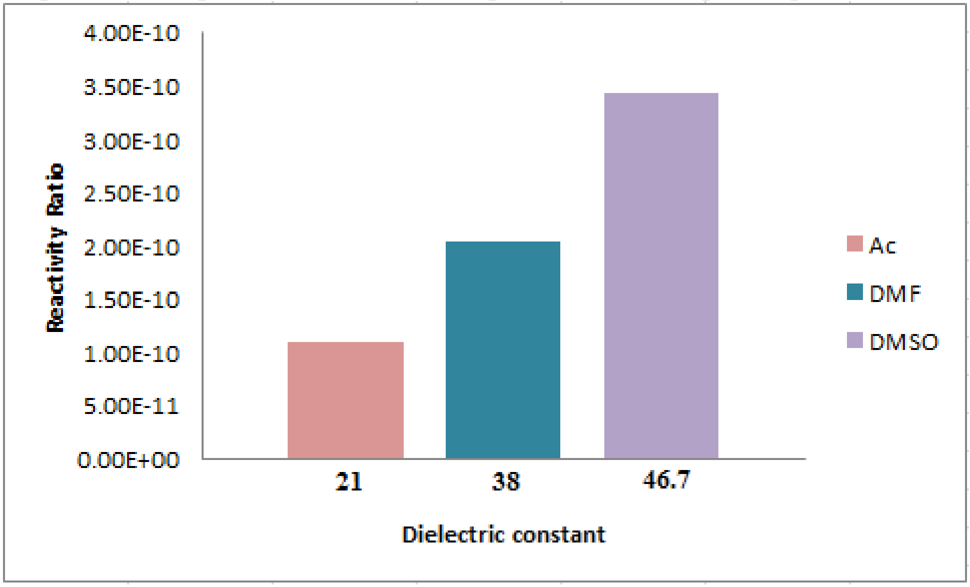


Figure (3): Variation in reactivity ratio with the dielectric constant of the solvent, for the photodecomposition of $Cr(L)_3$ complex in different polar aprotic solvents.

Table (2): Variation of natural logarithm plot of $Cr(L)_3$ complex with irradiation time in different organic solvents ($\lambda_{irr.}$ = 311 nm at 25 ^{0}C).

Irradiation Time	Solvents		
	DMSO	Ac	DMF
0	3.134	1.76	2.114
15	2.91	1.5	2.05
30	2.614	1.234	1.976
45	2.5	0.92	1.802
60	2.1	0.7	1.4

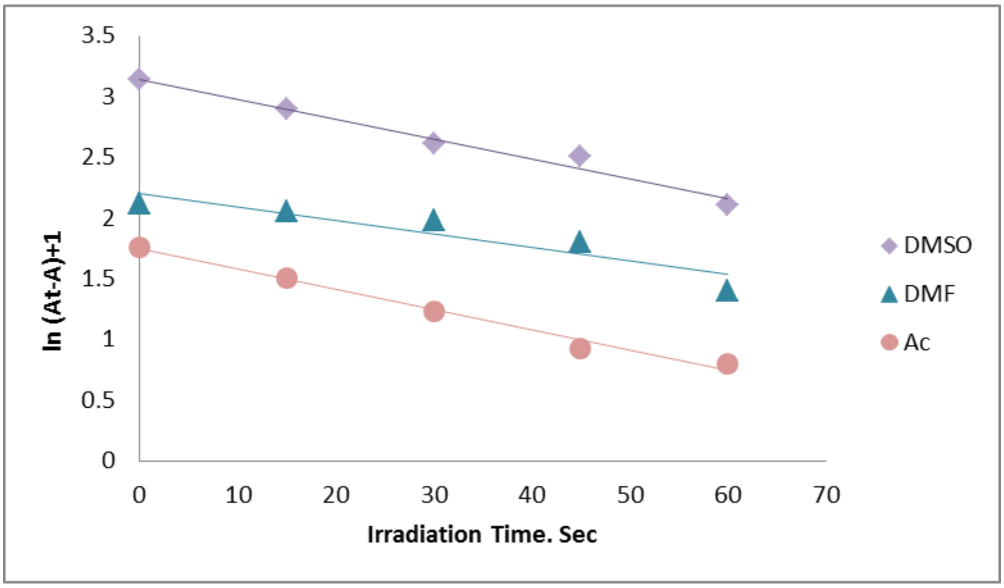


Figure (4): Variation of natural logarithm plot of $Cr(L)_3$ complex with irradiation time in different organic solvents ($\lambda_{irr.}$ = 311 nm at 25 ^{0}C).

Conclusions

In this work, the photochemical of chelate complex 2-(6-methoxynaphthalen-2-yl)propanoic acid chromium (III) $Cr(L)_3$ was studied in three polar aprotic solvents: dimethyl sulfoxide (DMSO), dimethylformamide (DMF), acetone (AC) were studied The quantum yield (Q_d), rate of photodecomption 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 > DMF > AC

Acknowledgements

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Abbreviations

Abbreviation	Full Meaning
AC	Acetone
D	Solvent molecule
DMSO	Dimethylsulphoxide
DMF	Dimethylformamide
HD	Solvent molecule
I_{Abs}	Light intensity
K_1	Rate constant of reaction(1)
K_{-1}	Rate constant of reverse reaction(1)
K_2	Rate constant of reaction(2)
K_3	Rate constant of reaction(3)
K_4	Rate constant of reaction(4)
K_5	Rate constant of reaction(5)
k_d	Specific rate constant for Cr(III)
Q_d	Quantum yield
L	2-(6-methoxynaphthalen-2-yl)propanoic acid

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