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### Kinetic study of photodecomposition of Oxo 1,1- dimethyl hydrazido-bis (dialkyl dithiocarbamato) molybdenum(VI)complex.

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#### ABSTRACT

The complex oxo 1,1-dimethyl hydrazido – bis (di alkyl dithiocarbamato) molybdenum (VI)[alkyl : methyl, ethyl] were prepared by mid complex dioxo bis (dialkyl dithiocarbamato) molybdenum and 1,1-di methyl hydrazine. The complex identified by FT-IR, UV. Vis spectroscopy, DSC measurements. Ethanolic solution complex was irradiation with UV light MPML for 90 min at 293K. Several conditions were studied such as concentration, time of irradiation, light intensity, pH value, solvent polarity and temperature . The reaction is pseudo first order and the dissociation of the complex was increased in case of : low of concentration and polarity of solvent and increasing of irradiation time, light intensity, pH value and temperature.

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#### INTRODUCTION

Molybdenum was discovered in 1778 by Scheele and prepared by Hjelm in 1782 but it was not pure (Tsigdinos and Moh., 1978) . It belong to transition elements falls in d-block in periodic table has the electronic configuration (Kr)<sub>36</sub> 5S<sup>1</sup>4d<sup>5</sup> in 6A (Sykes, 1987). It's found in earth shell about %10<sup>-4</sup> and found as molybdate salt (Douglas and Rao,2010), It can be prepared by oxidation of MoS<sub>2</sub> to MoO<sub>3</sub> then the late reduced by hydrogen to convert to Mo element (Rollinson,1975). It importance come from its wide applications like additive in alloy to improve the roughness and hardness for Iron and non corrosive nikel-iron alloy (Mellor and Longmans, 1959). It's used as hydro desulfurization agent in petrol industry (Pope, 1991).

The chemistry of oxo molybdenum is more extensive than another transition metal( Jeyakumar, and Chand, 2009). The commercial value of thiocarbamate compounds and its complexes with transition elements increased also the biological activity that attracted by researches has to study the chemical properties of these compounds (Coord, 2002) dithiocarbamate behave as a ligand mono dentate and bi dentate can bind with metal ion by one sulfur atom or both of them (Nabipour *et al*, 2010; Steggerda *et al*, 1981). These ligands stabilize the high valent state of metal ion like dioxo dithiocarbamato molybdenum (Moee and. Larson,

1967) and used in solar cell industry by conversion of solar to electric energy (Ghosh *et al*, 1998). These complex are added to gas oil as antioxidant to improve the performance of decrease the friction under high pressure and temperature during engine operation (Shah etal , 2012; Yan *et al*, 2012) di Oxo dithiocarbamato molybdenum compound react with dimethyl hydrazine to give the opposite complexes by reaction of N atom with Mo and these compounds have high stability (MacKay and Fryzuk, 2004; Carrroll, 1978) The aim of this research is preparation of di Oxo dithiocarbamato molybdenum and react with 1,1-dimethyl hydrazine to give Oxo 1,1 – dimethyl hydrazido – bis (dialkyl dithiocarbamato) molybdenum and identified by FT –IR analysis, UV- Vis spectroscopy and DSC measurements. The complex photo degradation would be studied under UV illumination at 366 nm and study the effected conditions like time of irradiate, concentration, light intensity, solvent and temperature.

#### Experimental:

##### Materials:

All material are used directly without any further purification absolute methanol, absolute ethanol, absolute isopropanol, absolute 1 – butanol (Scharlau purity 99.9%) dichloromethane (GGC purity 99.8%) diethyl ether (DFCL purity 99.5%) ammonium molybdate (B.D.H purity 99%) Sodium dimethyl

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dithiocarbamate, Sodium diethyl dithiocarbamate and 1,1- dimethyl hydrazine (Sigma Aldrich purity 99%) hydrochloric acid (Scharlau purity 99.9%) Sodium hydroxide (B.D.H).

Instruments:

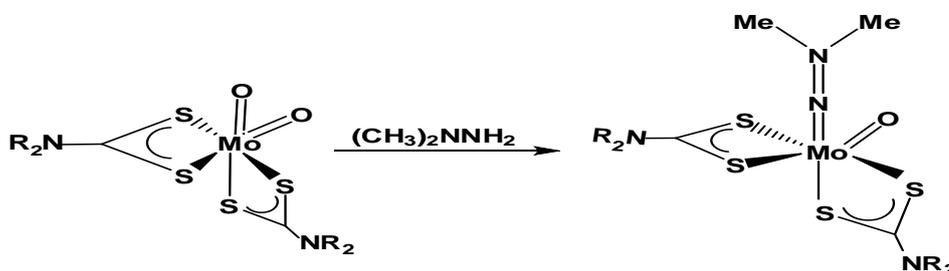
U.V- Vis spectrometer (UV-2601 Shimadzu-Japan), infrared spectrometer (FT-IR 8400S Shimadzu- Japan), the medium pressure mercury lamp (UVL-21San Gabriel – U.S.A), pH instrument (pHS -25CW HANNA- England), Oven (DIN-12880 Binder- Germany), light intensity (Dr - Honk made in Germany), a rotary evaporator (RE-200000 Stanforo – U.S.A), Thermo Circulator (LCB-R08 Labtech - Kora), DSC measurement (shimadzu-Japan).

*Irradiation system:*

3ml of complex ethanolic solution was irradiated in 1cm<sup>3</sup> quartz .The distance between lamp (MPML) and cell was 2 cm of circulating system to maintain a constant temperature when irradiation the highest intensity of the lamp at 366 nm with intensity of  $3.86 \times 10^{-9}$  ens . cm<sup>-2</sup> . sec<sup>-1</sup> .

Preparation Oxo complex 1,1 - Dimethyl hydrazido - Bis(dialkyl dithiocarbamato) molybdenum (VI):

0.7 g of MoO<sub>2</sub> (S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub>[R= Methyl , Ethyl] mixed with methanol then 0.1 gm of (1,1 -NNMe<sub>2</sub>) was added with stirring under reflux for is hour . rotary evaporator was used to reduce the solvent. The complex was re-crystallized in dichloromethane - diethyl ether and the complex was dark orange (Moore and Larson, 1967) The equation of preparation show in the following scheme (Karin, 2005). where R= Methyl or Ethyl.



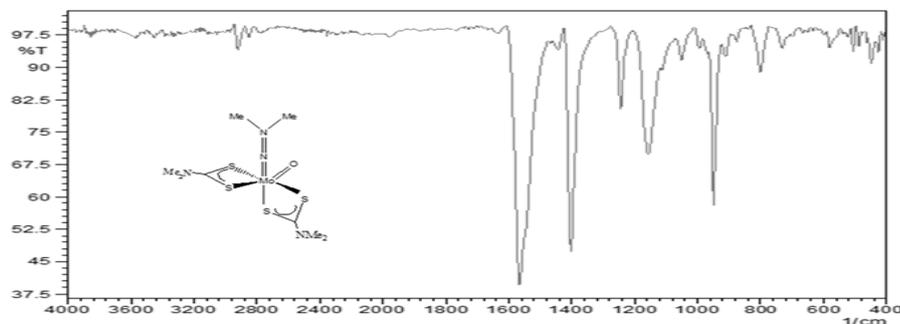
Scheme illustrates the compositional formula for the composition of the complex MoO(1,1-NNMe<sub>2</sub>)(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub>

## RESULTS AND DISCUSSION

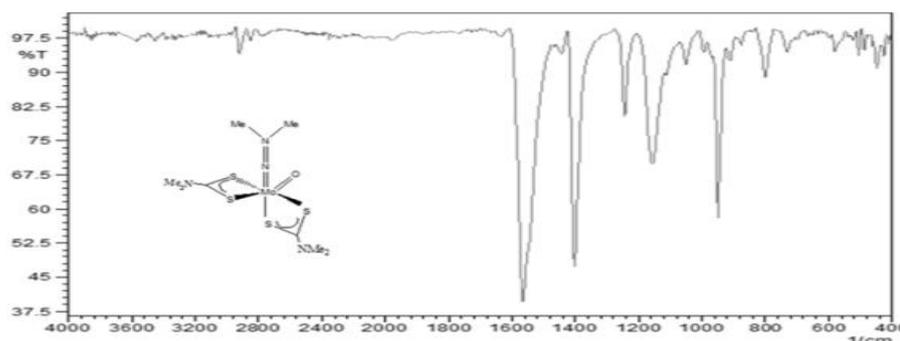
*FT – IR analysis:*

Figures (1,2) shows the infrared spectrum of the complexes under study it's found that there is a strong band absorption at (1516 , 1564 cm<sup>-1</sup>) belong to bond (C = N) and the absorption of medium intensity band at (1010, 995 cm<sup>-1</sup>) back to the vibration stretching of (C - S) bond (Abdul Muthalib, 2011; Galakhov *et al*, 1999 ) also appearance strong absorption band at (954, 947 cm<sup>-1</sup>) belong to the vibration frequency of the bond (Mo = O) (Jale Öcal,

2009) and the weak band at (579, 578 cm<sup>-1</sup>) belong to bond (Mo - S) appears as band within the range (1076-1207, 1049-1155 cm<sup>-1</sup>) belonging to the stretching vibration frequency of the bond (C = S) (Sofija *et al*, 2012) also showed medium intensity band (1276-1242 cm<sup>-1</sup>) belong to vibrate the bond (C -N)( Pavia *et al*, 2001) In addition to the appearance of strong bond at (800 cm<sup>-1</sup>) belong to the bond (Mo = N) and band at (1440-1400 cm) returning to the stretching vibration of (N = N) bond (Sharma *et al*, 2013) for complex 1, 2 respectively. Electronic spectrum of complex



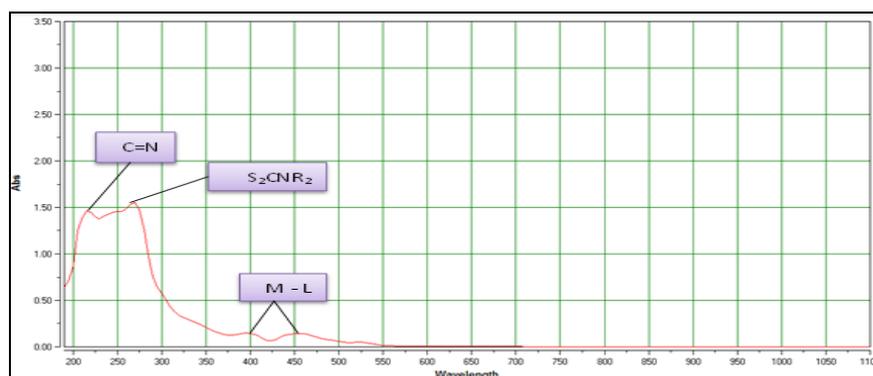
**Fig. 1:** The infrared spectrum of the complex MoO (1,1 -NNMe<sub>2</sub>) (S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>



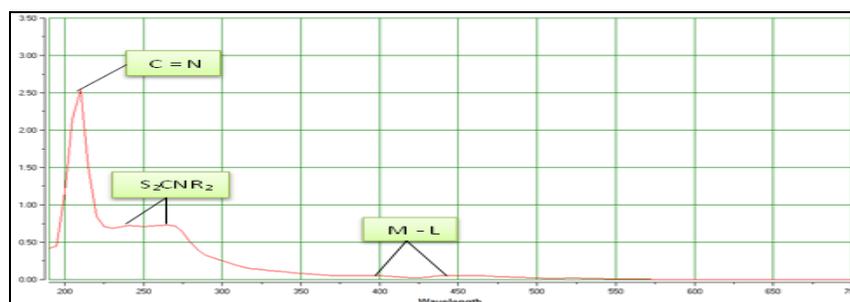
**Fig. 2:** The infrared spectrum of the complex MoO (1,1 -NNMe<sub>2</sub>) (S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub>

The electronic spectra is shown in Figures 3,4 two bands at 402-443 and 404-440 nm back to the electronic transitions of the type  $n - \pi^*$  (Sofija *et al.*, 2012) for complex 1 and 2 respectively because of overlapping hydrazine derivative to form the complexes under study . Absorptions at 217, 270

and 209, 240 – 266 nm respectively they belong to compensate the electronic transitions of the type  $\pi - \pi^*$  (Hasyiya *et al.*, 2013) of each of the ligand dialkyl dithiocarbamate and bond (C=N) respectively



**Fig. 3:** U.V – Visible spectrum the complex MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> at concentration of 40 ppm, pH = 7 and temperature of 283 K



**Fig. 4:** U.V – Visible spectrum the complex MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub> at concentration of 40 ppm , pH = 7 and temperature of 283 K

#### **Differential scanning calorimetry:**

DSC of complexes were examined and recorded between room temperature to 500 ° C almost to know melting point and thermal stability. According to

figures 5, 6 there is no clear melting and the complexes undergo several stage of decomposition and this result is common in dithiocarbamate complex with transition metals (Ahmad *et al.*, 2010)

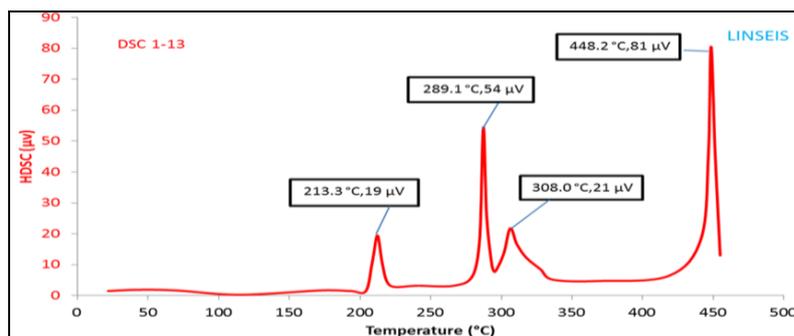


Fig. 5: Differential scanning calorimetry of complex  $\text{MoO (1,1-NNMe}_2\text{) (S}_2\text{CNEt}_2\text{)}_2$

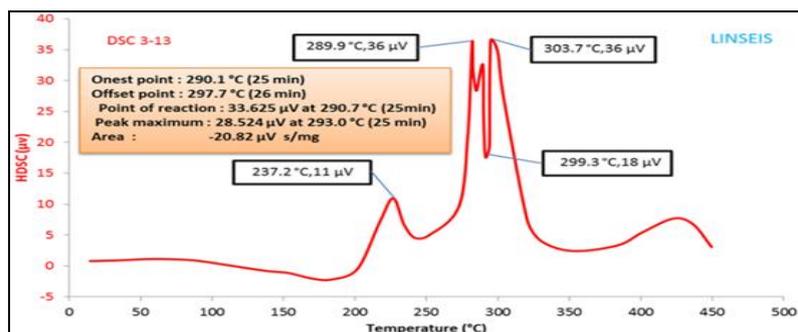


Fig. 6: Differential scanning calorimetry of complex  $\text{MoO (1,1-NNMe}_2\text{) (S}_2\text{CNMe}_2\text{)}_2$

**The effect of irradiation period:**

The study showed that the time of irradiation effect on the concentration of the complexes during the intervals between 0 - 90 minutes and the absorbance was measured at different wavelength,

where it was noted that the complexes absorption spectrum decreases with increasing time of irradiation as shown in Figures 7, 8 in all bands, but the band at 400 nm need less irradiation time in comparison with ether bands

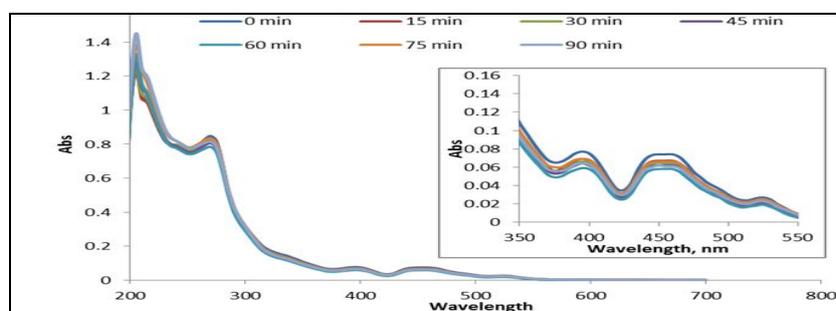


Fig. 7: U.V – Visible absorption spectrum at complex  $\text{MoO (1,1-NNMe}_2\text{) (S}_2\text{CNEt}_2\text{)}_2$  at a concentration of 40 ppm as a function of irradiation time at a temperature of 293 K , pH=7 and light intensity  $3.86 \times 10^{-9}$  ein  $\text{cm}^{-2} \text{sec}^{-1}$

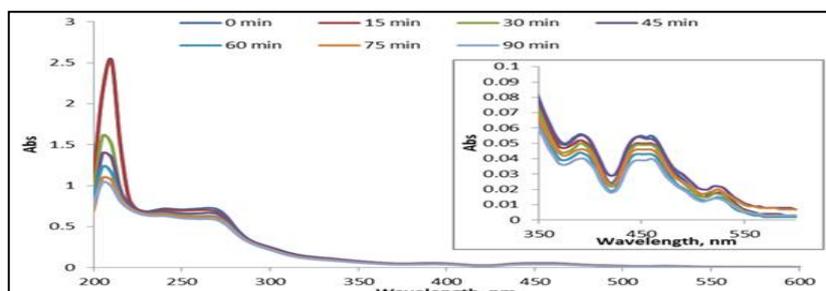
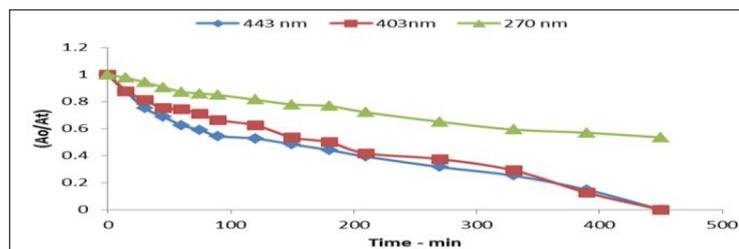
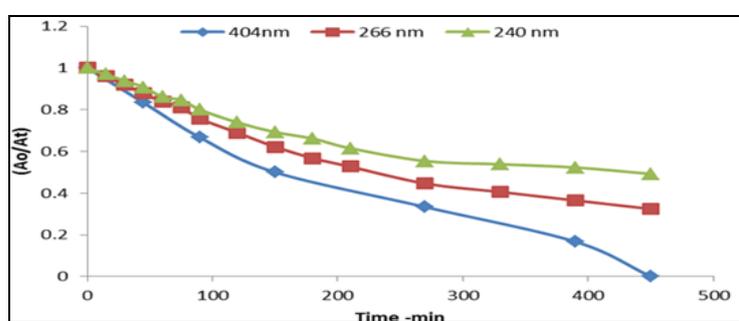


Fig. 8: U.V – Visible absorption spectrum at complex  $\text{MoO (1,1-NNMe}_2\text{) (S}_2\text{CNMe}_2\text{)}_2$  at a concentration of 40 ppm as a function of irradiation time at a temperature of 293 K , pH=7 and light intensity  $3.86 \times 10^{-9}$  ein  $\text{cm}^{-2} \text{sec}^{-1}$

Figures 9, 10 illustrates the effect of changing proceeding time of irradiation of the complexes where the dissociation of the entire complex in a period of time 450 minutes, and absorption in the ultraviolet region need longer periods of time to complete the dissociation.

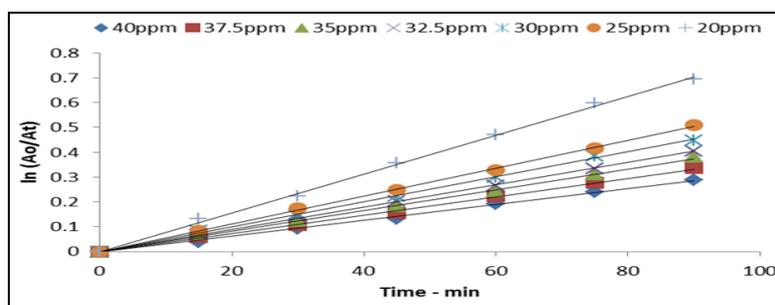


**Fig. 9:** the effect of the period of irradiation an the rate of the dissociation of the complex MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> at concentration of 40 ppm as a function of irradiation time at a temperature of 293 K, pH = 7 and light intensity  $3.86 \times 10^{-9}$  ein cm<sup>-2</sup>sec<sup>-1</sup>

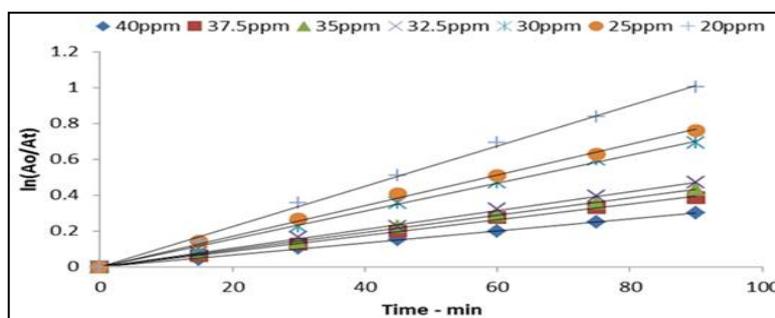


**Fig. 10:** the effect of the period of irradiation an the rate of the dissociation of the complex MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub> at concentration of 40 ppm as a function of irradiation time at a temperature of 293 K, pH = 7 and light intensity  $3.86 \times 10^{-9}$  ein cm<sup>-2</sup>sec<sup>-1</sup>

**Effect of concentration :** Figures 11 and 12 show the effect of concentration in the range (20 – 40) ppm was studied during 90 min. The rate of reaction was increasing when concentration decreased.

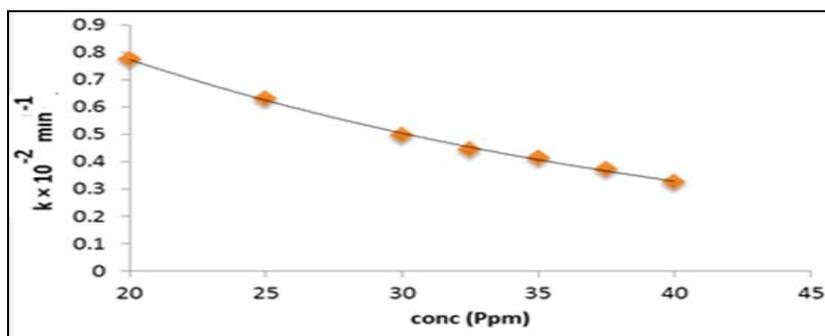


**Fig. 11:** the effect of concentration of the complex MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> on the dissociation at 293 K, pH = 7 and light intensity  $3.86 \times 10^{-9}$  ein cm<sup>-2</sup>sec<sup>-1</sup>,  $\lambda_{max} = 443$  nm

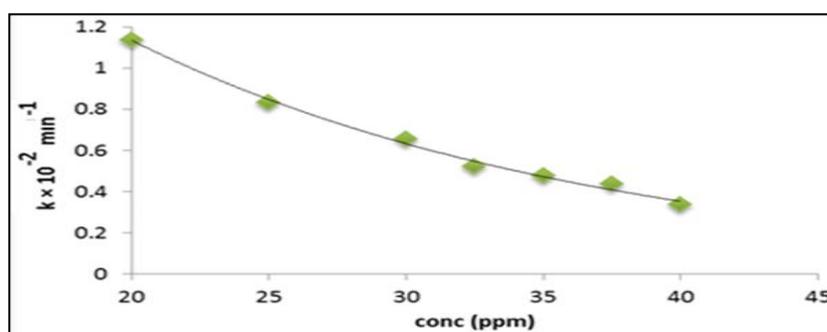


**Fig. 12:** the effect of concentration of the complex MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub> on the dissociation at 293 K, pH = 7 and light intensity  $3.86 \times 10^{-9}$  ein cm<sup>-2</sup>sec<sup>-1</sup>,  $\lambda_{max} = 404$  nm

According to first order of dissociation reaction the rate constant was obviously exponentially change with concentration (Junpei *et al*, 2006) as shown in figures 13, 14.



**Fig. 13:** the effect of concentration on the rate constant of the dissociation of the complex MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> at a temperature of 293 K, pH = 7 and light intensity  $3.86 \times 10^{-9} \text{ ein cm}^{-2} \text{ sec}^{-1}$ ,  $\lambda_{\text{max}} = 443 \text{ nm}$

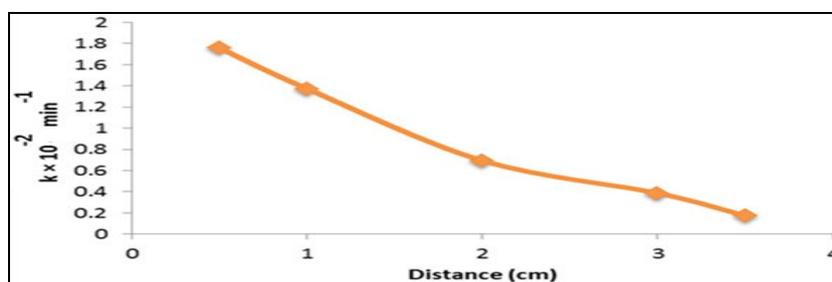


**Fig. 14:** the effect of concentration on the rate constant of the dissociation of the complex MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub> at a temperature of 293 K, pH = 7 and light intensity  $3.86 \times 10^{-9} \text{ Einstein .cm}^{-2} \text{ .sec}^{-1}$ ,  $\lambda_{\text{max}} = 404 \text{ nm}$

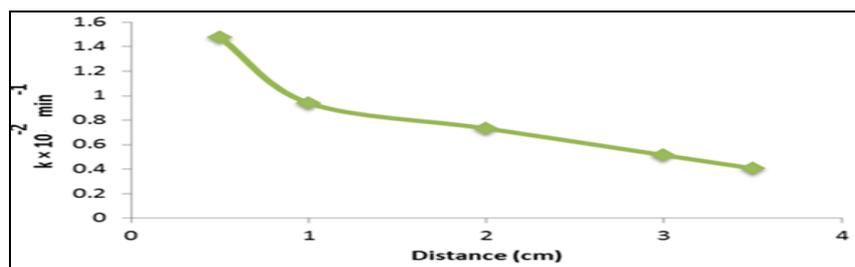
#### Effect of light intensity:

Follow-up study included the effect of changing the intensity of light flux on the dissociation of the complexes by changing the distance between the radiation source and the sample and the distance limited between 0.5 - 3.5 cm. figures 15, 16 shows the effect of light intensity on the rate constant on the

complex solution,. increasing the distance between the lamp and the sample (increasing light intensity) increasing the rate constant for dissociation because the number of photons that enter the solution is affected by the distance where the greater the intensity of any distance that increased the number of photons entering the solution (Salih, 1989).



**Fig. 15:** the effect of light intensity on the rate constant of the complex MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> dissociation at 40 ppm concentration, pH = 7 and temperature 293 K,  $\lambda_{\text{max}} = 443 \text{ nm}$

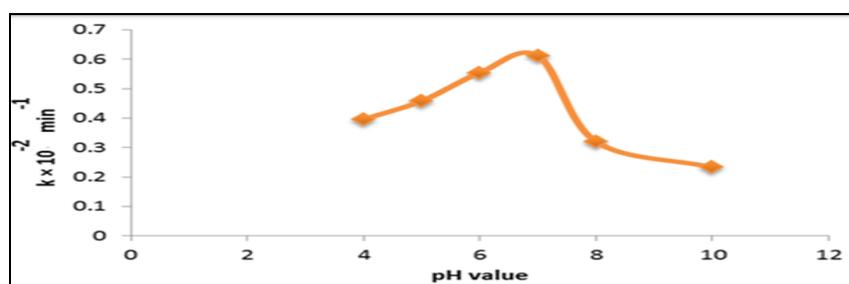


**Fig. 16:** the effect of light intensity on the rate constant of the complex MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub> dissociation at 40 ppm concentration, pH = 7 and temperature 293 K,  $\lambda_{\max}$  = 404 nm

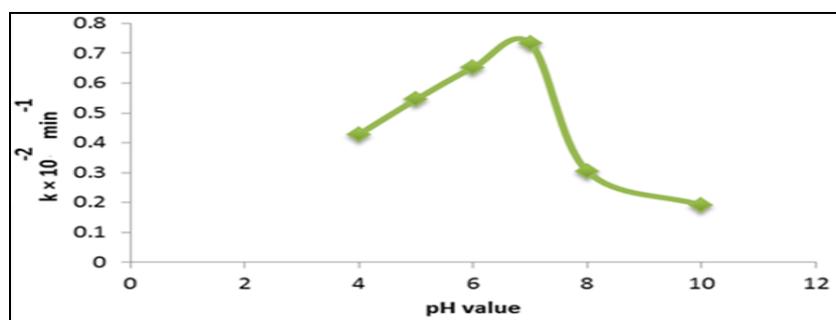
#### The effect of pH:

The effect of different values of the pH value were studied in the range 4-10 the higher rate of dissociation of the complexes when the pH 7 more

than basic and acidic solution (Kadhuim, 2012) figures 17, 18 show effect of changes in the values of pH on the rate constant of dissociation of the complex.



**Fig. 17:** the effect of the pH value on the rate constant of the dissociation of the complex MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> at 40 ppm concentration, temperature of 293 K and light intensity  $3.86 \times 10^{-9}$  ein cm<sup>-2</sup> sec<sup>-1</sup>,  $\lambda_{\max}$  = 443 nm



**Fig. 18:** the effect of the pH value on the rate constant of the dissociation of the complex MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub> at 40 ppm concentration, temperature of 293 K and light intensity  $3.86 \times 10^{-9}$  ein cm<sup>-2</sup> sec<sup>-1</sup>,  $\lambda_{\max}$  = 404 nm

#### Effect of Solvent:

The study included the effect four polar solvents on the rate constant of the dissociation of the complex and these solvents are methanol, ethanol, 1-butanol and isopropanol as it was found that the rate of the photolysis reaction as follows:

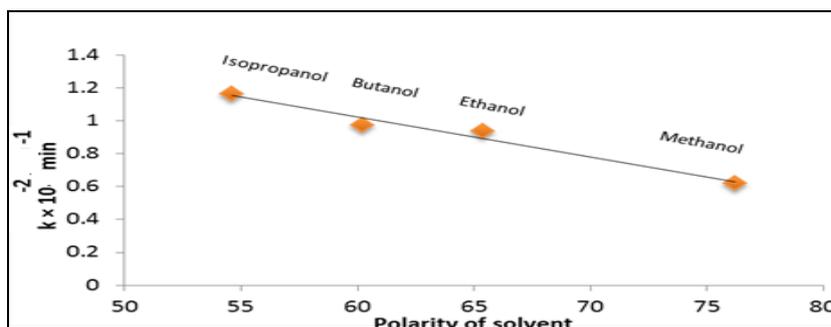
Isopropanol > 1- Butanol > Ethanol > Methanol

Through the results that have been reached we found that the rate constant of the dissociation of the complex decreased with increasing solvent polarity as shown in Table 1.

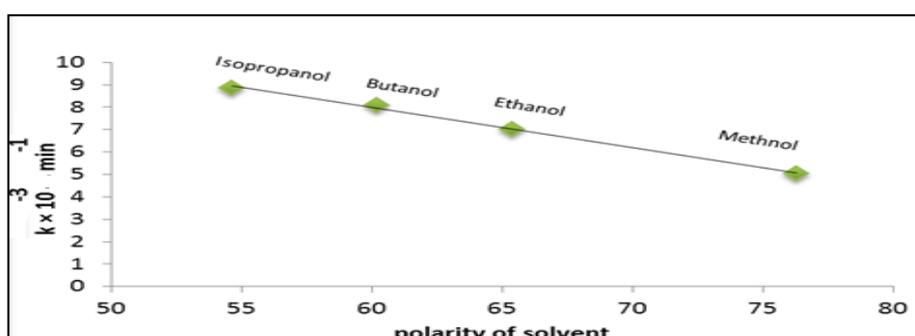
**Table 1:** the values of the rate constants for photolysis and solvent polarity

Isopropanol	1 - Butanol	Ethanol	Methanol	Solvent
54.6	60.2	65.4	76.2	Polarity(Smallwood, 1996)
1.16	0.97	0.93	0.61	K×10 <sup>-2</sup> min <sup>-1</sup> at 443 nm
8.86	8.08	7.00	5.03	K×10 <sup>-3</sup> min <sup>-1</sup> at 404 nm

Figures 19 and 20 show the relationship between the rate constants at photolysis of the complexes in different solvents.



**Fig. 19:** the effect of the solvent polarity on the rate constant of dissociation of the complex MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> at 40 ppm concentration, pH = 7, temperature of 293 K and light intensity  $3.86 \times 10^{-9} \text{ ein cm}^{-2} \text{ sec}^{-1}$ ,  $\lambda_{\text{max}} = 443 \text{ nm}$

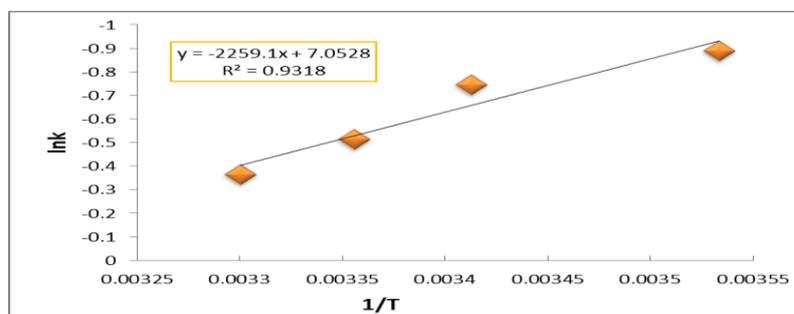


**Fig. 20:** the effect of the solvent polarity on the rate constant of dissociation of the complex MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub> at 40 ppm concentration, pH = 7, temperature of 293 K and light intensity  $3.86 \times 10^{-9} \text{ ein cm}^{-2} \text{ sec}^{-1}$ ,  $\lambda_{\text{max}} = 404 \text{ nm}$

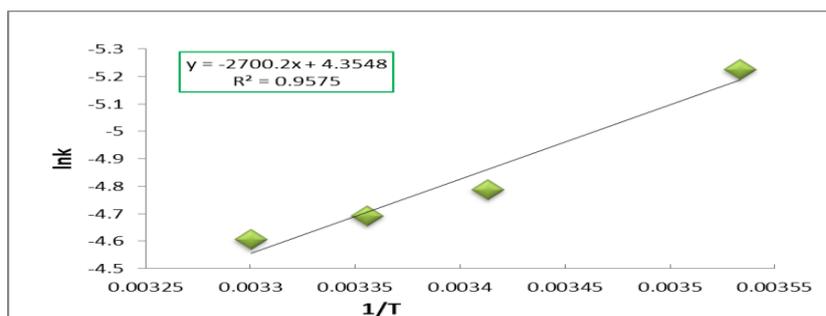
#### Effect of temperature:

The study included the effect of temperature range between 283-303 K on the rate of the dissociation of the complexes. It was found that the temperature rise increases the rate of the dissociation of the complex, and that the increase in temperature leads to an increase in the generation of free radicals, which affect "directing" in the rate constant (Obies, 2011). From equation of Arrhenius extract the value

of the activation energy, when drawing relationship between the inverted temperature  $1/T$  and  $\ln k$  we get a straight line slope is equal to  $-E_a/R$  as in Figures 21, 22 and the calculated activation energy of the complexes. It was found that the activation energy of MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> and MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub> are 18.782, 22.188 KJ / mole respectively.



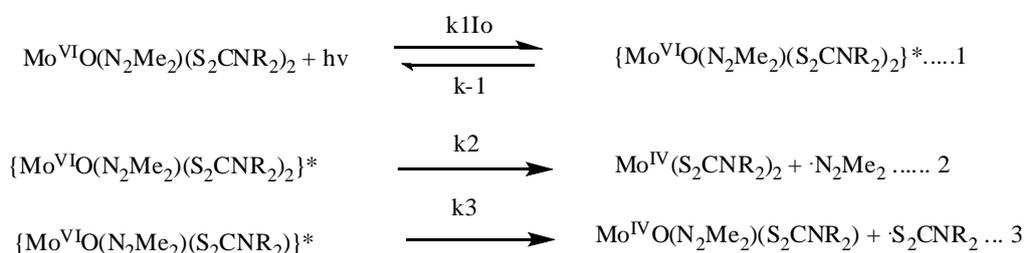
**Fig.21:** Arrhenius equation for the dissociation of the complex MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> at 40 ppm concentration, pH = 7, light intensity  $3.86 \times 10^{-9} \text{ ein cm}^{-2} \text{ sec}^{-1}$ ,  $\lambda_{\text{max}} = 443 \text{ nm}$



**Fig. 22:** Arrhenius equation for the dissociation of the complex MoO (1,1-NNMe<sub>2</sub>) (S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub> at 40 ppm concentration, pH = 7, light intensity  $3.86 \times 10^{-9}$  ein cm<sup>-2</sup> sec<sup>-1</sup>,  $\lambda_{\max} = 404$

#### Proposed mechanism of photodecomposition:

Photodecomposition of the complex was studied and suggested mechanism in the light of previous studies (Habeeb, 2005) as the equation (1) represents the absorption of the complex at wavelength 366 nm, which leads to the transferring of the complex from steady-state to the excited state, and to remove the excitation energy may be deactivated or the complex dissociates :



Where : R : Methyl or Ethyl group

The equation (2) and (3) is a propagation stage and Mo reduced (+6) to (+4) oxidation (Yoshihisa *et al*, 1986) through the loss of a molecule di alkyl hydrazine as in equation (2) or loss of a dimethyl dithiocarbamate in equation (3) and the ligands are liberated as free radicals (Hussain, 2014).

#### Conclusions:

The complex oxo 1,1-dimethyl hydrazido – bis (di alkyl dithiocarbamate) molybdenum (VI)[alkyl : methyl, ethyl] were prepared by mid complex dioxo bis (dialkyl dithiocarbamate) molybdenum and 1,1-di methyl hydrazine successfully. The complexes are thermally stable and have no clear melting point. Photodecomposition of complexes follow pseudo-first order reaction, so they need at least 8 hours to decompose. The pH value effect inversely at above and beneath 7 and polarity when decreased the rate was high. The activation energy was low at visible light measurement than uv measurement.

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