OPTIMAZATION OF PHOTODECOPOSITION OF CHELATE COMPLEXES DINITRO PHENYL HYDRAZEDO-TRIS (DIMETHYL DITHIOCARBAMATO) MOLYBDENUM (V) AND 2, 4-DINITRO PHENYL HYDRIZEDO-TRIS (DIMETHYL DITHIOCARBAMATO) MOLYBDENUM (V)

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ABSTRACT

This research includes the preparation and spectral identification of two complexes [Mo (N_2Ph) ($S_2CNMe_2)_3$] - and [MoN_2Ph-($NO_2)_2(S_2CNMe_2)_3$]-by using UV-Vis and FTIR spectra. The kinetics of chemical decomposition of two complexes were studied by irradiation of complexes solutions at λ = 365 nm and 25°C for 60 min in ethanol. It has been found the decomposition follow first order kinetics, as well as calculated the rate constant of photo decomposition reaction k_d by observing the spectral changes during the process of irradiation. To optimization conditions of decomposition, it is necessary to study the effect of several factors on the photochemical behavior which included: effect of concentration, light intensity, temperature, pH, solvent, and effect of gas. The mechanism of complex decomposition has been interpreted that there is redox- reaction has been happening in two complexes.
Keywords: photodecomposition, Molybdenum, 2, 4-dinitro phenyl hydrazedo, dimethyl dithiocarbamat, Chelate complexes.

INTRODUCTION

Molybdenum has a large number of cases in oxidative compounds ranging from -II to VI as well as it has a coordination number ranging from 4-8, which led to having a variety of stereo chemistry[1]. There is an element in the earth's crust molybdenum amount is estimated at 10^{-4}%, where there is usually as molybdate salts, molybdenum quantity existing in the soil and the plant has become a significant factor in the research and studies in recent years[2]. Thereby became molybdenum for many applications in a varied and wide area, including dyes[3], corrosion inhibitors[4], fume suppressants[5], additives for lubricants[6], as well as in the manufacture of fertilizer[7].
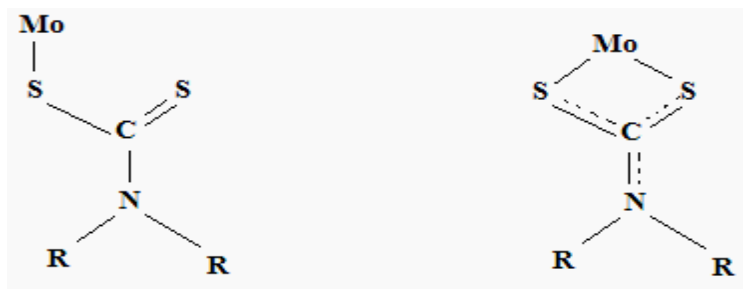

Fig.-1: Forms of dithaiocarbamat anion

Dithaiokarbamat complexes used with a large number of transition metal elements.[8-12] This ligand can show high stability under a variety of oxidative and coordinate situations. Also, the study of geometry for

this ligand could indicate significant changes in the chemical behavior when associating it with the metal ions and the formation of complexes, dithaiocarbamat anion exhibits the behavior of monodentate or bidentate, as shown in Figure-1.[13]

There are many applications for this ligand complex with molybdenum, where it can be used as corrosion inhibitor, antioxidants additives, and friction modifiers which can effectively reduce wear and friction in the boundary lubrication.[14-16]

There have been several recent studies according the reactivity of dinitrogen coordinated to transition metal ions.[17,18] These ligands can act as monodentate or bidentate, as shown in this formula:[19]

$$Mo\text{-}N=N\text{-}R \qquad Mo=N\text{-}NR_2$$
$$\text{Dizenido(1-)} \qquad \text{Hydrazido(2-)}$$
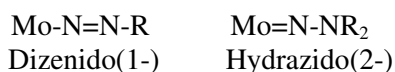
EXPERIMENTAL

Chemicals and Instruments

All chemicals were used without further purification, Phenyl Hydrazine 99% (Sigma), absolute Methanol, Ethanol, Isopropanol, 1- butanol (all 99%, Scharlau), Sodium diethyl dithiocarbamat 99% Sigma), Ammonium molybdat 99% (Sigma). Spectrometer FT-IR8000 series, UV-1650 (Shimadzu), Low pressure mercury lamp LLE-1 (Lambda), pH meter 211-Instrument (Hanna).

The photolysis apparatus

The photolysis apparatus setup is shown in Fig.-2 which involve a low pressure mercury lamp fitted with a power supply and emits UV light in the wavelength range 365 - 579 nm, the light was passed through a filter to transmit it predominately of wavelength 365 nm, this filter fixed on a hole created in thermostat water bath made from black painted glass. The lamp is turned on for 10 minutes before started of Irradiation of samples.
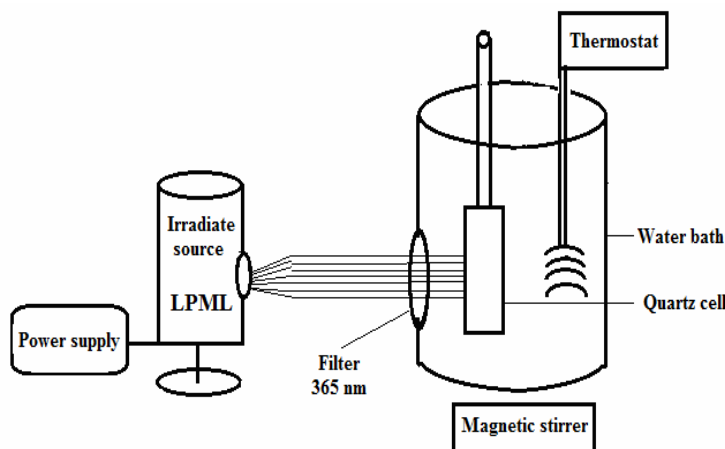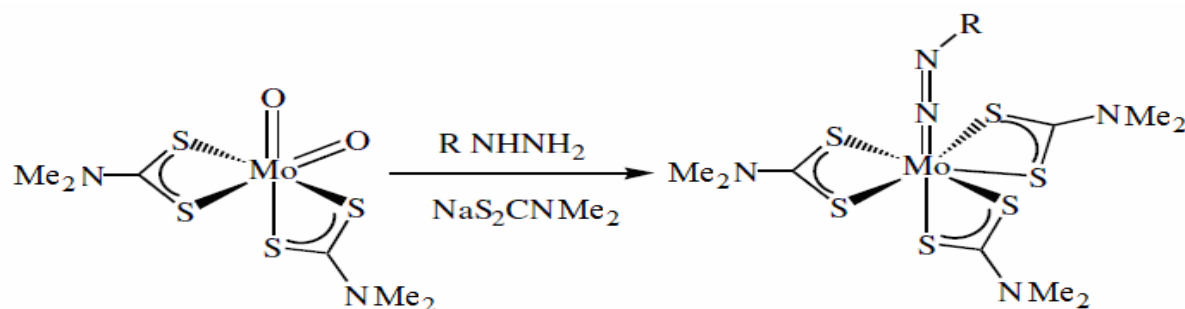

Fig.-2: parts of photolysis apparatus

Preparation of complexes

The complexes [Mo (N$_2$Ph) (S$_2$CNMe$_2$)$_3$] and [MoN$_2$Ph-(NO$_2$)$_2$(S$_2$CNMe$_2$)$_3$] (Complexes-1 and 2 respectively) have been prepared as reported by Moore and Larson,[20] the following equation shows the preparation of the complexes:

Where R = Phenyl, 2,4-di Nitro phenyl groups

Scheme-1

Light intensity Measurements

Light intensity was measured by chemical actinometer Potassium ferrioxalate $K_3Fe(C_2O_4)_3$ as Hatchard and Parker proposed method.[21]

RESULTS AND DISCUSSION

Infrared Spectra

The infrared spectroscopic data of the two complexes have been studied and shows strong bands had been observed at 1388cm^{-1} and 1319cm^{-1} to υ (C-N) bond, and medium band at 995 cm^{-1} and 918 cm^{-1} due to υ (C-S) bond[22,23], The strong absorption bands at 1473 cm^{-1} and 1434 cm^{-1} due to azo group υ (N=N), The spectra of complexes shows another absorption bands at 1149cm^{-1} and 1134cm^{-1} due to combined bond υ (N…C…S)[24]. Also the short absorption bands in printed fingers area at 586 cm^{-1} and 555 cm^{-1} due to (Mo-S), and bands in 856cm^{-1} and 831cm^{-1} due to (Mo-N).[25,26] Fig.-3 and Fig.-4 show the infrared spectra of two complexes.
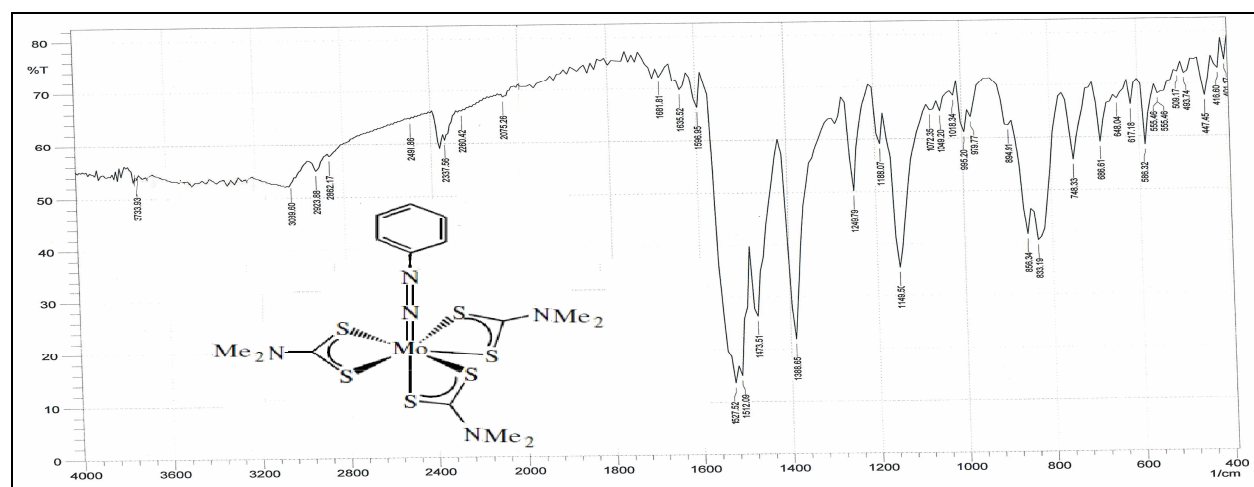

Fig.-3: Infrared spectrum of [Mo (N₂ph) (S₂CNMe₂)₃]

Electronic Spectra

The electronic Spectra of the complexes 1 and 2 were studied in absolute ethanol as a solvent (2.5x10^{-5}M). The complex1 spectrum gives two absorption bands were detected first band located at 404 nm for n→π* transition of the (Mo-N) and (C=S), the second band observed at 251 nm due to π→π* transitions of the dithiocarbamat and phenyl groups in the phenyl hydrazido legand. The complex2 spectra gives three absorption bands, this band showed a red shift because of the substitution on phenyl group, first

band located at 515 nm for n→π* transition of the (Mo-N) and (C=S), second bands observed at 303 nm due to π→π* transitions of dithiocarbamat and third bands observed at 226 nm due to π→π* transitions of phenyl groups in phenyl hydrazido legand.[23,27] Figure-5 shows the electronic spectra of the two complexes.
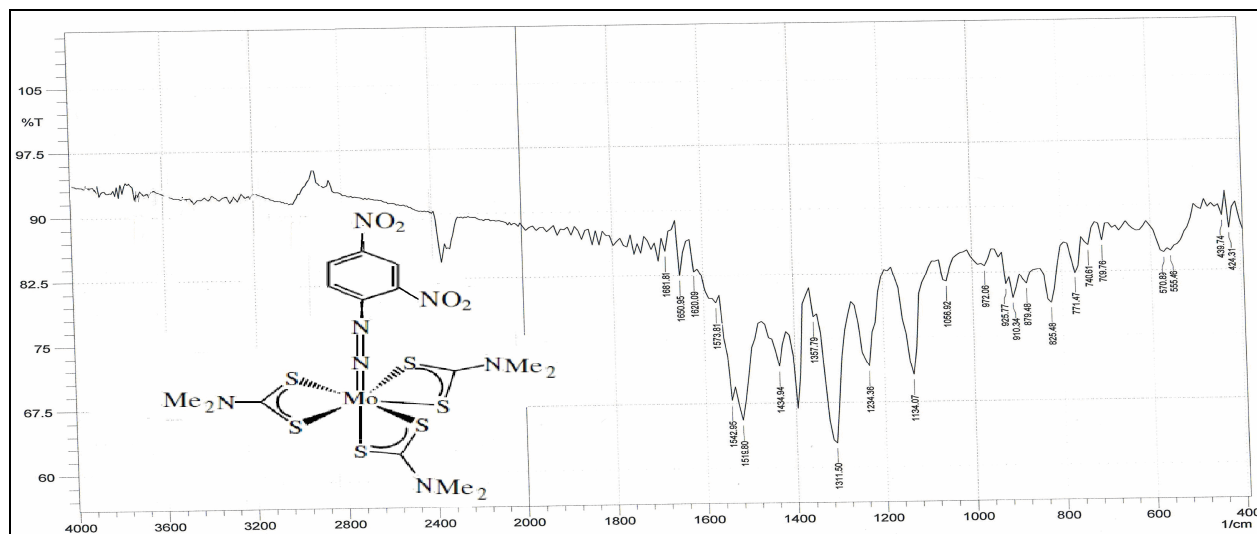

Fig.-4: Infrared spectrum of [MoN$_2$Ph-(NO$_2$)$_2$(S$_2$CNMe$_2$)$_3$]
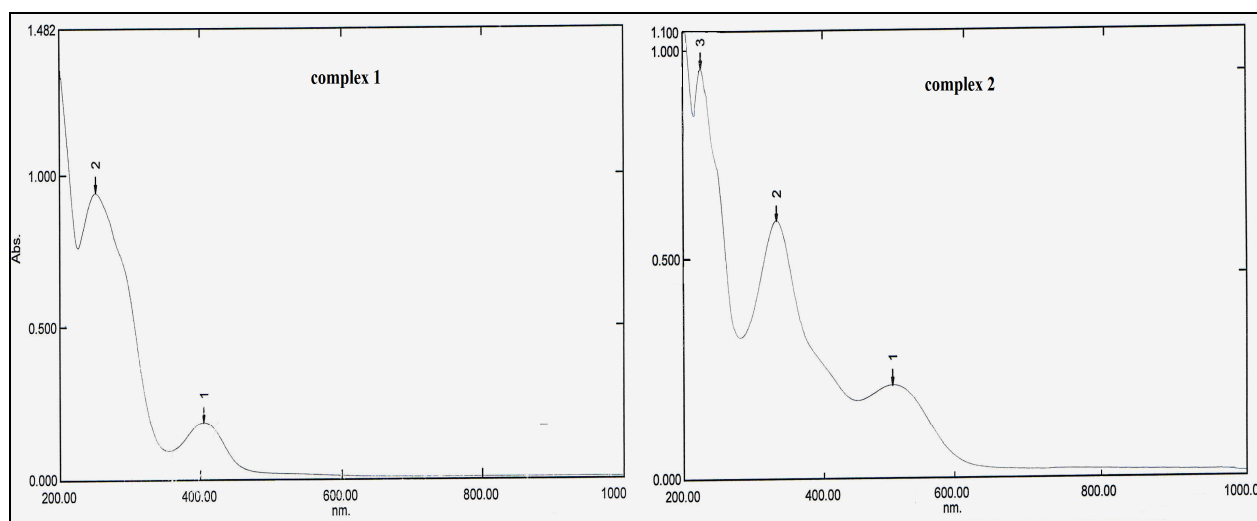
Fig.-5: Electronic spectrum of [Mo (N$_2$ph) (S$_2$CNMe$_2$)$_3$] and [MoN$_2$Ph-(NO$_2$)$_2$(S$_2$CNMe$_2$)$_3$] complexes.

The effect of irradiation time and complex concentration

The absorbance was measured during the period time rang between 0-60 min, noting that the absorption spectra when all wavelengths was below with an increase of the irradiation time, the results are shown in Fig.-6.
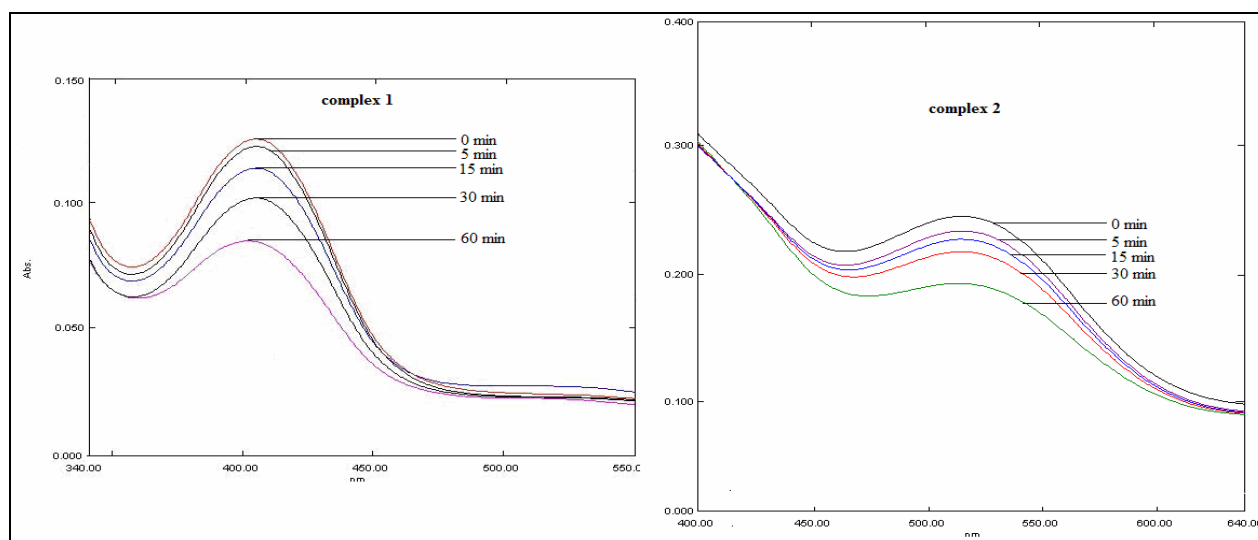
Fig.-6 :Absorption UV-vis spectra to[Mo(N$_2$ph)(S$_2$CNMe$_2$)$_3$] and [MoN$_2$Ph-(NO$_2$)$_2$(S$_2$CNMe$_2$)$_3$] 2.5x 10^{-5} M as a function of irradiation time at 298 K , pH = 7 , I$_o$ = 1.63x10^{-5} ein.L^{-1}.sec^{-1}.

Figure-7 shows the effect of the change in the time of irradiation on complexes absorbance, were shows the low absorption at irradiation continues**.**
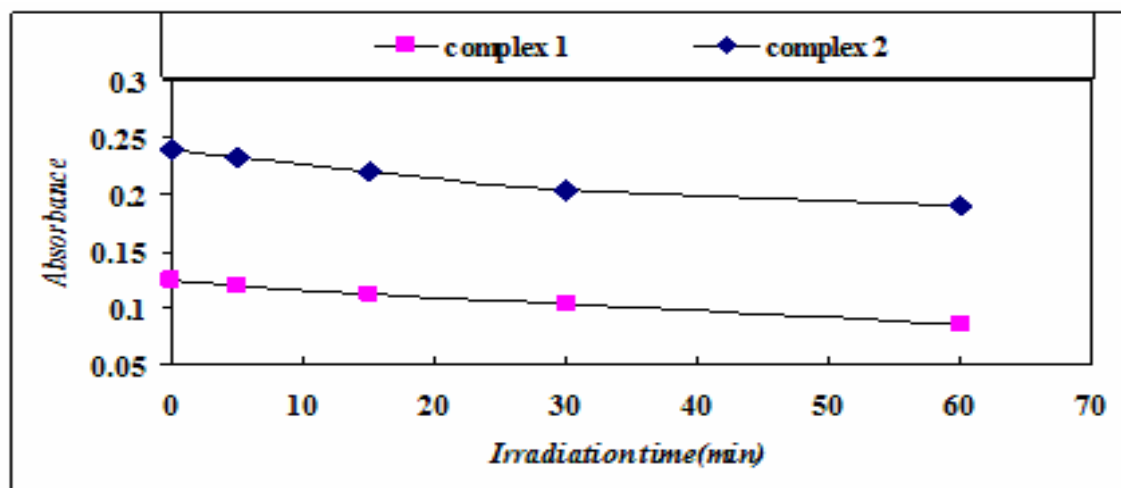

Fig.-7 :Effect the time of irradiation on the decomposition rate of [Mo(N$_2$ph)(S$_2$CNEt$_2$)$_3$] and [MoN$_2$Ph-(NO$_2$)$_2$(S$_2$CNMe$_2$)$_3$] at 2.5x 10^{-5} M, 298 K , pH = 7 , I$_o$ = 1.63x10^{-5} ein.L^{-1}.sec^{-1}.

The rate constant of decomposition was determined by the following first - order equation:[28,29]

$$\ln (A_t - A_\infty) = \ln (A_0 - A_\infty) - k_d t \qquad (1)$$

The plot of ln (A$_t$ - A$_\infty$) with irradiation time gives a straight line, which indicates that the reaction is first-order as shown in Fig.-8.
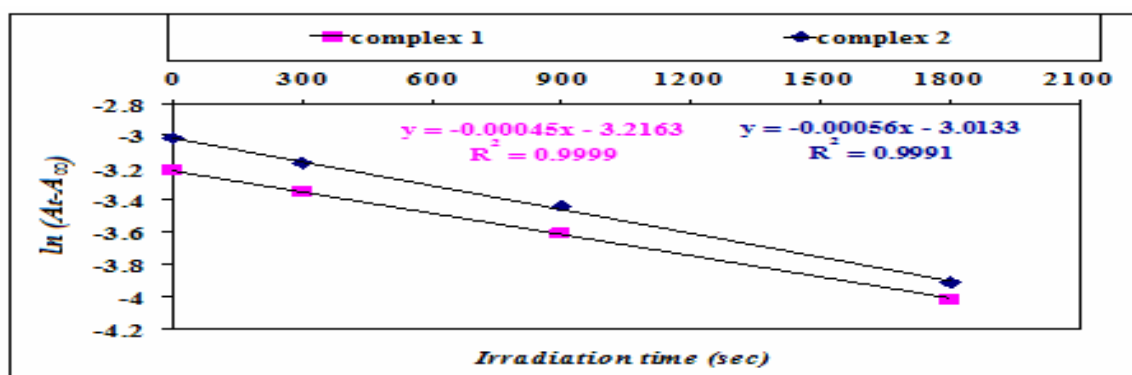
Fig.-8: The relation between irradiation time and ln $(A_t - A_\infty)$ of the complex [Mo (N_2ph) $(S_2CNEt_2)_3$] and [MoN$_2$Ph-$(NO_2)_2(S_2CNMe_2)_3$] at 2.5x 10^{-5} M, 298 K, pH = 7, I_o = 1.63x10^{-5} ein.L^{-1}.sec^{-1}.

Effect of Light Intensity

The impact of the change in the incidence light intensity on the decomposition rate was studied by changing the distance between the radiation source and the irradiated sample.[30]

In general, it's found when the light intensity decrease, the decomposition rate also decreased. Table-1 shows the values of change in the incidence light intensity (I_0) and decomposition rate constant for the complexes.

Table-1: The values of incidence light intensity (I_0) and decomposition rate constant for the complexes [Mo (N_2ph) $(S_2CNEt_2)_3$] and [MoN$_2$Ph-$(NO_2)_2(S_2CNMe_2)_3$] at 2.5x 10^{-5} M, 298 K, pH = 7.

I_o x10^5 (ein.L^{-1}.sec^{-1})	K_d x (10^3 s^{-1})	
	Complex 1	Complex 2
1.63	0.43	0.59
1.59	0.34	0.50
1.52	0.28	0.45
1.41	0.23	0.31

Effect of Temperature

Experiments were performed on the complex within the range 293-303K. It has been found that its increasing temperature leads to increase in the decomposition rate. The increase in temperature leads to an increase in the rate of generation of free radicals, which affects the "direct" on the rate of interaction. Using the Arrhenius equation to illustrate the relationship between the decomposition constant rate and temperature. It is drawing this relationship was calculated activation energy of the complex and the results are shown in Fig.-9.

$$k = A\, e^{(-Ea/RT)} \tag{2}$$

Where k = rate constant of decomposition (sec^{-1}), A=frequency factor, R=gas constant = 8.314 J / mol. K., T= temperature in Kelvin.

Found that the activation energy of decomposition equal 24.808 kJ/mole for complex1 and 20.209 kJ/mole for complex-2.

Effects of acidic function

This study includes the effect of different values of pH within the range 3-11; the results show that the higher rate of complex decomposition was obtained at pH 11. The reason is the thiocarbamat radical

resulting from the photo decomposition reaction of the complex, able to combination with the same radical and formation thiol group as shown in the following equation.[31]
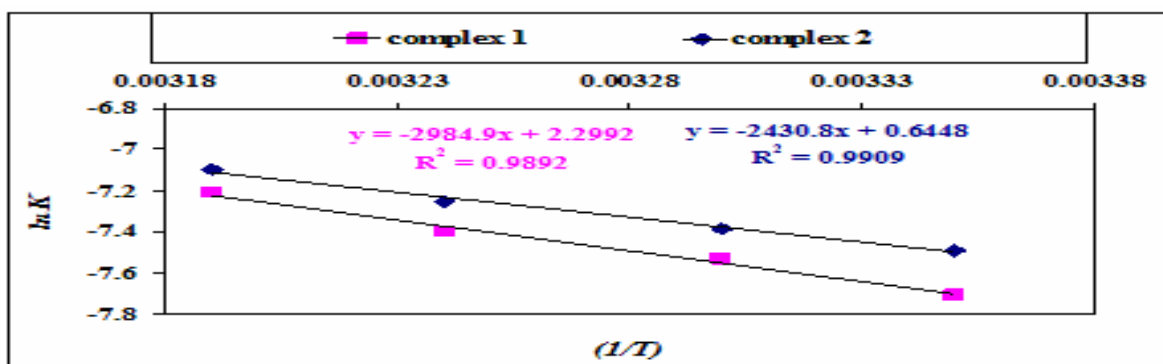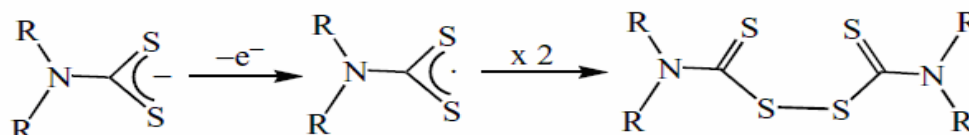

Fig.-9: Arrhenius equation to decomposition of the complex [Mo (N$_2$ph) (S$_2$CNEt$_2$)$_3$] and [MoN$_2$Ph (NO$_2$)$_2$(S$_2$CNMe$_2$)$_3$] at 2.5x 10^{-5} M, pH = 7 and I$_o$ = 1.63x10^{-5} ein.L^{-1}.sec^{-1}.

Scheme-2

Thiol compound may be decomposed in basic media and formation a negative ions, increasing of reaction rate as shown in the following equation.[32]

$$(R_2NCS_2)_2 + 2OH^- \rightarrow R_2NCS_2^- + R_2NCOS^- + H_2O + S^0 \qquad (3)$$

Figure-10 is shown the Effect of changing of pH value on the decomposition rate constant.
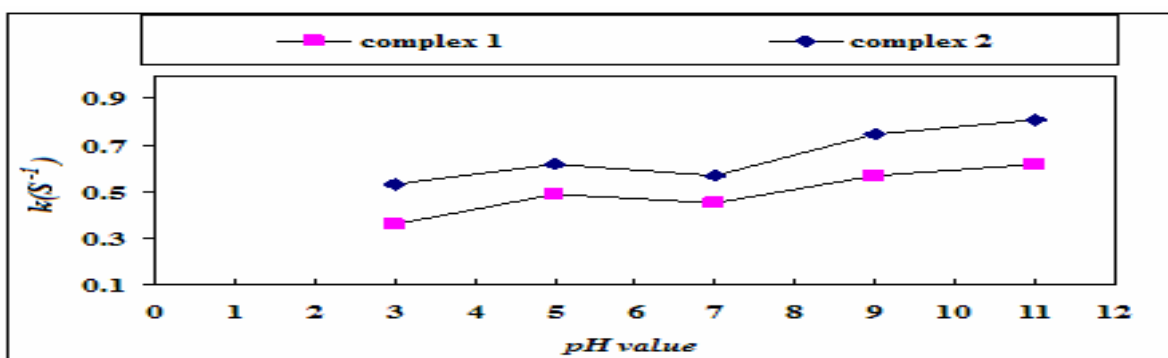
Fig.-10: Effect of pH on decomposition rate constant of [Mo (N$_2$ph) (S$_2$CNEt$_2$)$_3$] and [MoN$_2$Ph-(NO$_2$)$_2$(S$_2$CNMe$_2$)$_3$] at 2.5x 10^{-5} M, 298 K and I$_o$ = 1.63x10^{-5} ein.L^{-1}.sec^{-1}.

Effect of solvent

The effect of four polar solvents on the decomposition has been studied, using solvents methanol, ethanol, 1-butanol and isopropanol.

The results that have been getting it was found that the rate of decomposition increase with the increasing polarity of the solvent[33] as shown in Table-2.

Table -2: The relationship between solvent polarity and decomposition rate constant.

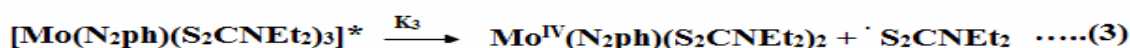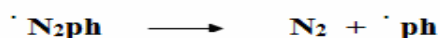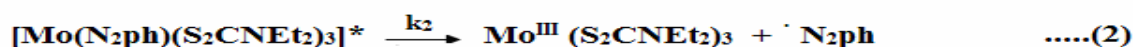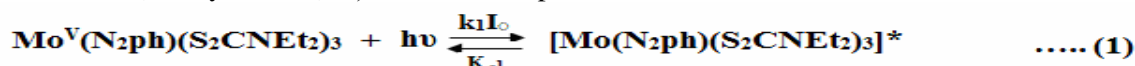| Solvent	Polarity	K_d x (10^3 s^{-1})	
		Complex 1	Complex 2
Methanol	76.2	0.51	0.64
Ethanol	65.4	0.45	0.56
1- butanol	60.2	0.41	0.51
Isopropanol	54.6	0.36	0.46

Effect of gas

The effect of different on the decomposition of the complex was studied, using gases nitrogen, air and oxygen. and found that the decomposition rate of the complexes increases according to the following order, as shown in Table-3.

Table- 3: the relationship between type of gas and the rate constant of complex decomposition.

Gas	K_d x (10^3 s^{-1})	
	Complex 1	Complex 2
Oxygen	0.59	0.7
Air	0.53	0.63
Without gas	0.45	0.56
Nitrogen	0.37	0.47

The mechanism of the photo decomposition of the complex Phenyl hidrazedo-tris (diethyl dithiocarbamato) Molybdenum) V) has been interpreted[34,35] as-

$$Mo^V(N_2ph)(S_2CNEt_2)_3 + h\upsilon \xrightarrow[K_{-1}]{k_1I_o} [Mo(N_2ph)(S_2CNEt_2)_3]^* \qquad \ldots\ldots (1)$$

$$[Mo(N_2ph)(S_2CNEt_2)_3]^* \xrightarrow{k_2} Mo^{III}(S_2CNEt_2)_3 + \cdot N_2ph \qquad \ldots\ldots(2)$$

$$\cdot N_2ph \longrightarrow N_2 + \cdot ph$$

$$[Mo(N_2ph)(S_2CNEt_2)_3]^* \xrightarrow{K_3} Mo^{IV}(N_2ph)(S_2CNEt_2)_2 + \cdot S_2CNEt_2 \qquad \ldots\ldots(3)$$

Scheme-3

Where step-1 represents complex absorption of light at 365 nm, which leads to the transmission of the complex molecule from non-excited state to the excited state. To get rid of the excitation energy may be the interaction go back to case basis, or may the complex decomposition as a result of process of splitting the bond metal - ligand leading to reduced molybdenum(V) to molybdenum(III) and molybdenum(IV), and formation free radical from separated ligand as shown in steps-2,and 3.

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