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Photodecomposition of molybdenum(II) and tungsten(II) carbonyl complexes with triazole, benz-imidazole, and oxadiazole acetylinic derivatives

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Abstract

Photodecomposition of 10 different molybdenum and tungsten mixed carbonyl complexes, $[M(CO)_3(B)(A)]I_2$ where B = *o*-phenanthroline or bipyridyl, A = 3-(2-propynyl)thio-4,5-diphenyl-4H-1,2,4-triazole (TRZA) or *S*-propynyl-2-thio benz-imidazole (BIMDA) and 2(2-propynyl-thio(5-phenyl)-1,3,4-oxadiazole (OXA). $M(CO)_3(TRZA)I_2$, $[M(CO)_2(PPh_3)_X(TRZA)I_Y]I_Z$ where $M = Mo$, X, Y and $Z = 1$ and $M = W$, X and $Z = 2$, $Y = 0$, have been performed at 365 nm in oxygen saturated chloroform at 25 °C. The absorbance spectrum of these complexes have been recorded with the time of irradiation in order to examine the kinetics of photodecay.

The apparent rate constant (K_d) for the first-order reaction have been calculated and found to be $(3.32–4.79) \times 10^{-5}\,s^{-1}$. The primary quantum yields (Φ) has also been calculated and were in the range $(8.33–12.1) \times 10^{-4}$. The mechanism of the photodecomposition has been suggested according to the kinetic, and photoproduct analysis data, and is similar to reaction of photo-oxidative degradation of polluted molecules in the water. © 2002 Published by Elsevier Science B.V.

Keywords: Photodecomposition; Molybdenum; Tungsten; Carbonyl complexes

1. Introduction

Metal carbonyl complexes are among the most photoreactive transition metal complexes known [1]. Metal carbonyls are numerous [2] and have studied the excited state processes and photoprocess including electronic energy phenomena [1,2]. Transition metal carbonyl complexes have been the object of photochemical investigations including group VIB metals. At the present time, correlations between electronic structures and reactivity are in primitive stages of development, therefore the organization of material is according to the central metal involved [2–4]. It appears that there is no definitive data to show that either photo-oxidation or photoreduction of primary photoprocess upon UV or visible excitation [2,4].

One has to consider reactions involving CO and a ligand. An emerging class of photoreactions of metal carbonyls is the fragmentation reaction of clusters as indicated in Eq. (1), and photo-oxidation of metal carbonyls to fragmentation as in Eq. (2) [5,6]:

$$[M(CO)_X]_n \xrightarrow{h\nu} M(CO)_X + [M(CO)_X]_{n-1} \tag{1}$$

$$M(CO)_n L \xrightarrow[{[O]}]{h\nu} M_X O_Y + CO + \text{ligand degradation to stable ions} \tag{2}$$

According to the electronic spectra of the excited states of these molecules, it can be seen that these contain a number of transitions in the visible region associated with ligand field, metal ligand charge transfer, ligand metal charge transfer absorptions, the intensity and wavelength depend on the type of metal atom and ligand [7,8]. In this work we used the following mixed ligand carbonyl complexes as examples for studying the photodegradation in the chloroform solvent.

Some metal carbonyl complexes may be used for the following applications:

1. photochemical conversion and storage of solar energy, as photosensitizer in hydrogen production from water splitting [9];
2. photo-oxidation degradation of complexes [5];
3. photoinitiation of polymerization cross-linking of polymers [10,11];
4. photostabilization of polymers, and photoinduces for polymer degradation [12];
5. photocatalysts for organic synthesis [13–15a];
6. gasoline octane number improver [15b].

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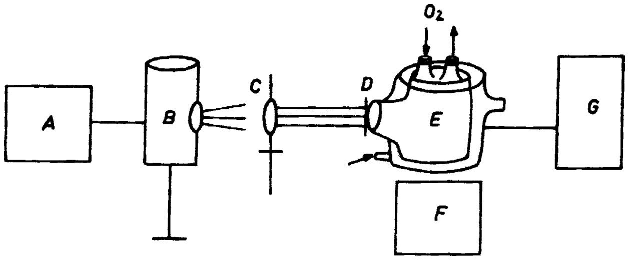

Fig. 1. Schematic diagram of the experimental apparatus for photolysis of complexes: (A) power supply unit; (B) MPML medium pressure mercury lamp; (C) lenses; (D) filter (365 nm); (E) quartz cell; (F) magnetic stirrer; (G) circulating water thermostat.

2. Experimental

Chemicals. (a) $K_3[Fe(C_2O4)_3]\cdot 3H_2O$ actinometer was prepared by the method reported by Hatchard and Parker [16]; (b) the metal carbonyl complexes (1–10) have been prepared as reported earlier [17]; (c) the chloroform used was of spectroscopic grade.

Experimental techniques. The photolysis apparatus used is shown in Fig. 1.

The photolysis of mixed ligand carbonyl compounds have been performed using a medium pressure mercury lamp. UV–Vis spectral absorption bands were obtained using Pye-Unicam (8700) spectrophotometer at 25 °C using chloroform as a solvent in quartz photochemical cell. A known concentration of the complex was introduced into the cell after treatment with oxygen for 20 min. The cell was closed tightly and the absorption spectra were recorded between 200 and 600 nm.

The measurement of the incident light (I_0) was carried out by using standard method of potassium ferrioxalate actinometry [16]:

$$I_0 = \frac{AV_1}{\varepsilon \Phi_\lambda V_2 t}$$

where I_0 is the incident light intensity, A the absorption at 510 nm, V_1 the final volume (25 ml), ε the extinction coefficient = slope of calibration curve, Φ_λ the quantum yield = 1.21 at 365 nm, V_2 the volume taken from irradiation solution (1 ml) and t the time of irradiation of actinometer solution (s).

3. Result and discussion

3.1. The spectra of mixed carbonyl complexes

UV–Vis spectra for the named complexes have been found to contain absorption bands around 365 nm as shown in Fig. 2 as a representative example. The molar extinction coefficient of these new compounds in chloroform have been measured and the data are tabulated in Table 1.

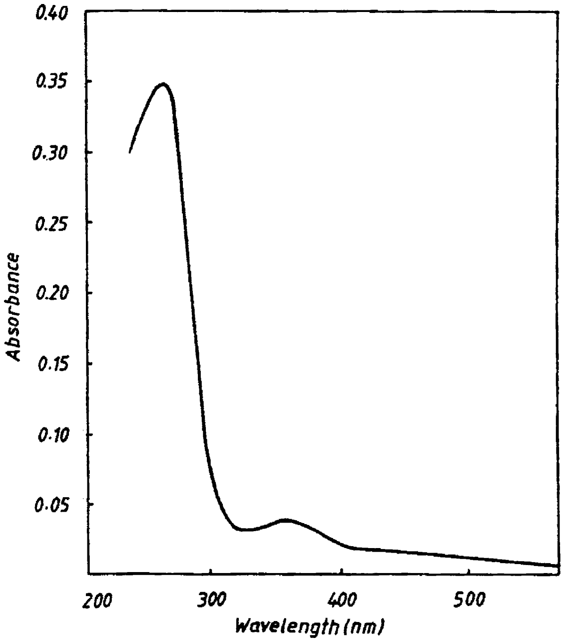

Fig. 2. Electronic absorption spectra of cation $[W(CO)_3(bp)(TRZA)]^{2+}$.

The ε values are around $(0.04–0.07) \times 10^{-5}$ mol^{-1} l cm^{-1} and are due to the π–π^* transition of the ligand in the complexes. The values are relatively high because this electronic transition is allowed, and is similar to values of other metal carbonyl complexes reported in literature [2,4].

The changes in absorbance during photolysis were measured for different irradiation periods of time at 365 nm in order to study the kinetics of the photodecay of complexes in solution. To measure the absorbance at infinite time (A_∞) the solution was irradiated for at least 10 h.

The specific decomposition rate constant of each complex (K_d) was determined after examining the order of reaction of these carbonyl compounds. For example the spectra of the cation $[W(CO)_3(bipy)(TRZA)]^{2+}$ (Fig. 3), treated kinetically by plotting the curve between OD, log OD and 1/OD versus irradiation time as shown in Fig. 4 (Table 2).

Only the plot of log OD with irradiation time gives a straight line, which indicates that the reaction is first-order.

Table 1
Values of molar extinction coefficient for mixed ligand metal di- and tri-carbonyl complexes at 365 nm (ε)

Compound no.	Compounds	ε ($\times 10^{-5}$ mol^{-1} l cm^{-1})
1	$[W(CO)_3(bipy)(TRZA)]I_2$	0.0518
2	$[Mo(CO)_3(bipy)(TRZA)]I_2$	0.0493
3	$[W(CO)_3(o\text{-}phen)(TRZA)]I_2$	0.0666
4	$[Mo(CO)_3(o\text{-}phen)(TRZA)]I_2$	0.0498
5	$[W(CO)_2(PPh_3)_2(TRZA)]I_2$	0.05393
6	$[Mo(CO)_2(PPh_3)(TRZA)I]I$	0.0773
7	$[W(CO)_3(TRZA)I_2]A$	0.0510
8	$[Mo(CO)_3(TRZA)I_2]A$	0.0499
9	$[W(CO)_3(bipy)(BIMDA)]I_2$	0.0591
10	$[W(CO)_3(bipy)(OXA)]I_2$	0.0661

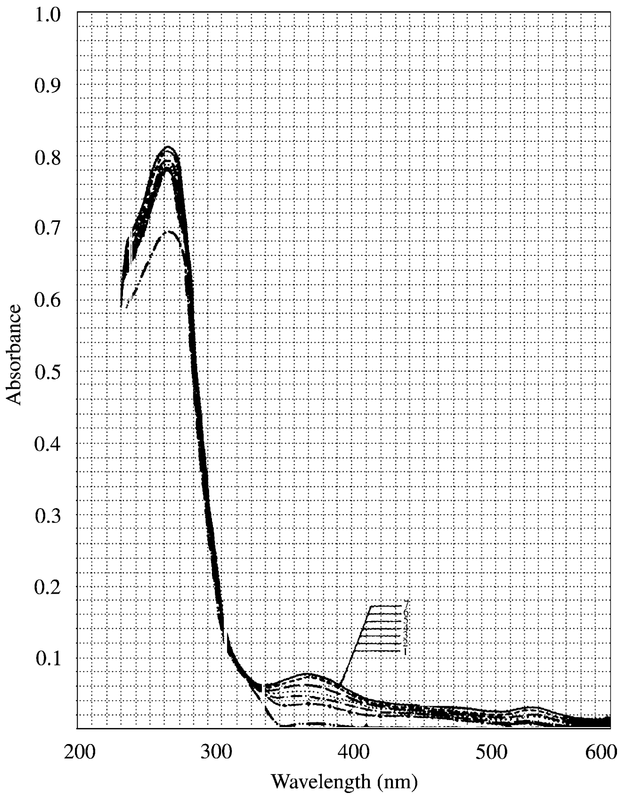

Fig. 3. Electronic absorption spectra of cation $[W(CO)_3(bp)(TRZA)]^{2+}$. Spectral changes at 356 nm accompanying change in irradiation time in chloroform solvent at 298 K. (1) 0, (2) 60, (3) 120, (4) 180, (5) 240 (6) 300 and (7) 360 min.

Table 2
Absorbance of cation $[W(CO)_3(bipy)(TRZA)]^{2+}$ versus irradiation time

$A_{365\,\mathrm{nm}}$	$(A_\infty - A_t)$	$\log(A_\infty - A_t)$	$(A_\infty - A_t)^{-1}$	Time (min)
0.004	0.099	−1.101	12.658	0
0.032	0.051	−1.2924	19.607	60
0.042	0.041	−1.3870	24.390	120
0.050	0.033	−1.4814	30.30	180
0.062	0.020	−1.6980	50.00	240
0.068	0.015	−1.821	66.66	300
0.083	0	0	0	360

Table 3
Specific rate constant (K_d) for mixed ligand metal di- and tri-carbonyl compounds

Compound no.	Rate constant, K_d ($\times 10^{-5}\,s^{-1}$)
1	3.8977
2	4.3746
3	4.1222
4	4.16032
5	3.46429
6	3.31579
7	3.91104
8	4.79696
9	3.7246
10	3.65397

The K_d of decomposition of this complex was determined by the following first-order equation:

$$\ln(A_\infty - A_t) = \ln A_\infty - K_d t$$

The value of K_d for this complex is $3.89 \times 10^{-5}\,s^{-1}$. Photolysis of other complexes (2–10) have been performed in a similar manner. Figs. 5–8 show the change in UV–Vis spectra with time of irradiation.

The order for these photodegradation reactions has determined for all complexes using log OD as a function of time. The plots show that all other carbonyl compounds are first-order. The results of rate constants have been treated by least mean square and are given in Table 3 for all mixed ligand carbonyl compounds.

It seems that the values of rate constant K_d (apparent rate constant) for all studied carbonyl compounds are low and similar $(3.315–4.797) \times 10^{-5}\,s^{-1}$, which are in the range of photodegradation or mineralization of large heterogenous organic molecules containing N, O, P using oxygen of peroxide [18]. The kinetic analysis of the order of these photoreactions shows partial zero-order in some complexes, but the photoreactions of these complexes are in homogenous system, so it is considered to be first-order.

On irradiation of the complex (1) in chloroform the color changes gradually from colorless to pale yellow and as

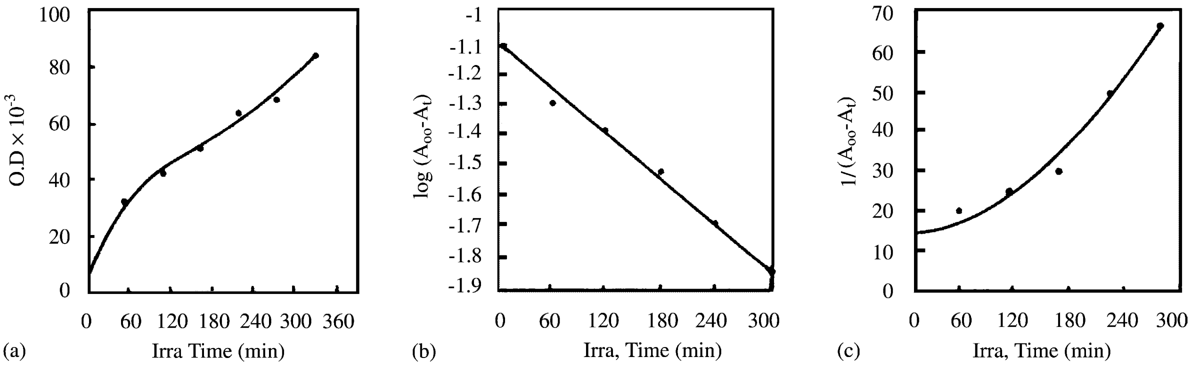

Fig. 4. (a–c) Variation of neutral logarithm of optical density with irradiation time of complex (1) in chloroform solvent ($\lambda_{irra} = 365$ nm at 298 K).

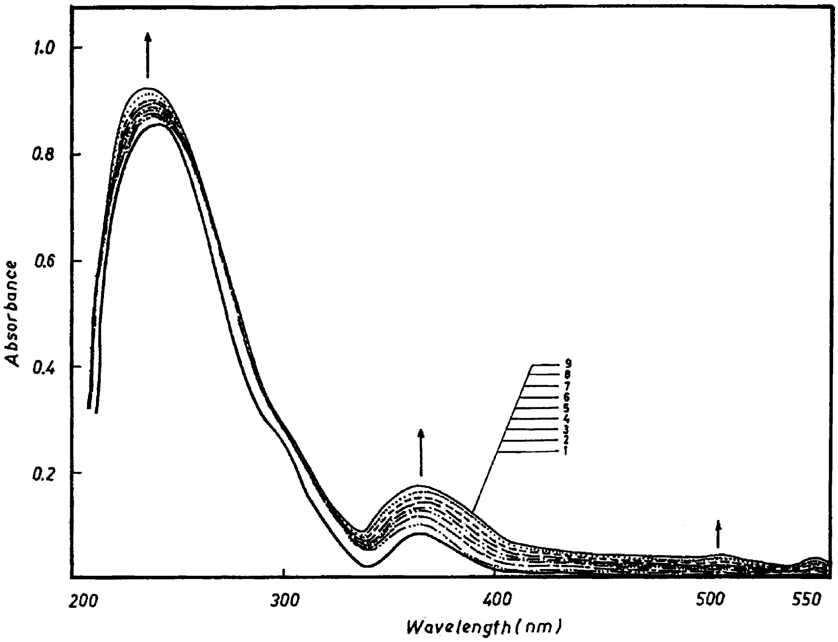

Fig. 5. Electronic absorption spectra of cation [$Mo(CO)_2(PPh_3)(TRZA)I$]I. Spectral changes at 365 nm accompanying change in irradiation time in chloroform solvent at 289 K. (1) 0, (2) 60, (3) 120, (4) 180, (5) 240, (6) 300, (7) 360, (8) 420 and (9) 480 min.

expected the UV spectrum changes with irradiation time (Fig. 3). There is an increase in the absorbance intensity of all bands with time of irradiation in the region 200–500 nm at low concentration of compound (2.532×10^{-5} M).

The absorbances of these bands were measured with time of irradiation. Other complexes (2–10) have been irradiated and treated in the same manner, the results are shown in Figs. 5–8 which are found to be similar to that of complex (1), and we may assume that in general, all photochemical change in these complexes are reactively similar and simple. Although we believe that our solvent undergoes photolysis during irradiation but this fact does not affect the change in spectra of the complex.

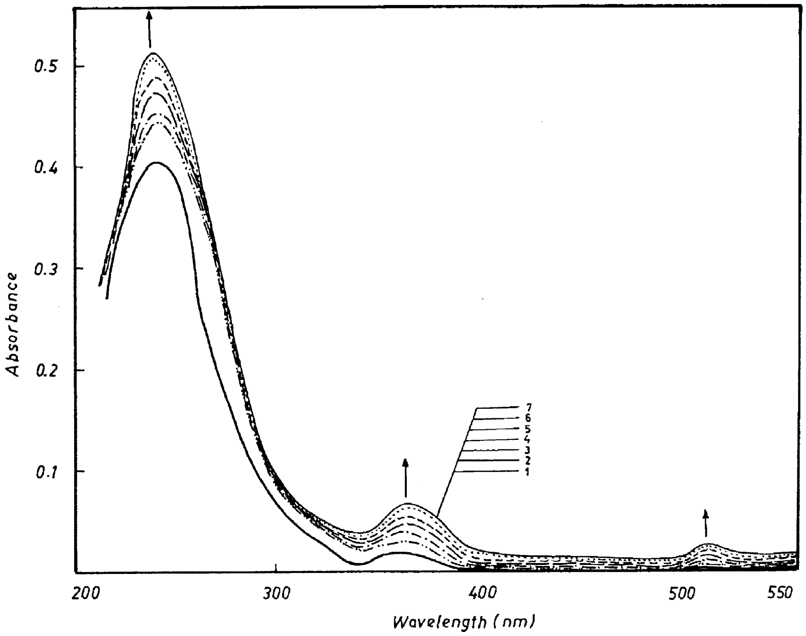

Fig. 6. Electronic absorption spectra of cation [$W(CO)_2(PPh_3)(TRZA)$]$^{2+}$. Spectral changes at 365 nm accompanying change in irradiation time in chloroform solvent at 289 K. (1) 0, (2) 60, (3) 120, (4) 180, (5) 240, (6) 300 and (7) 360 min.

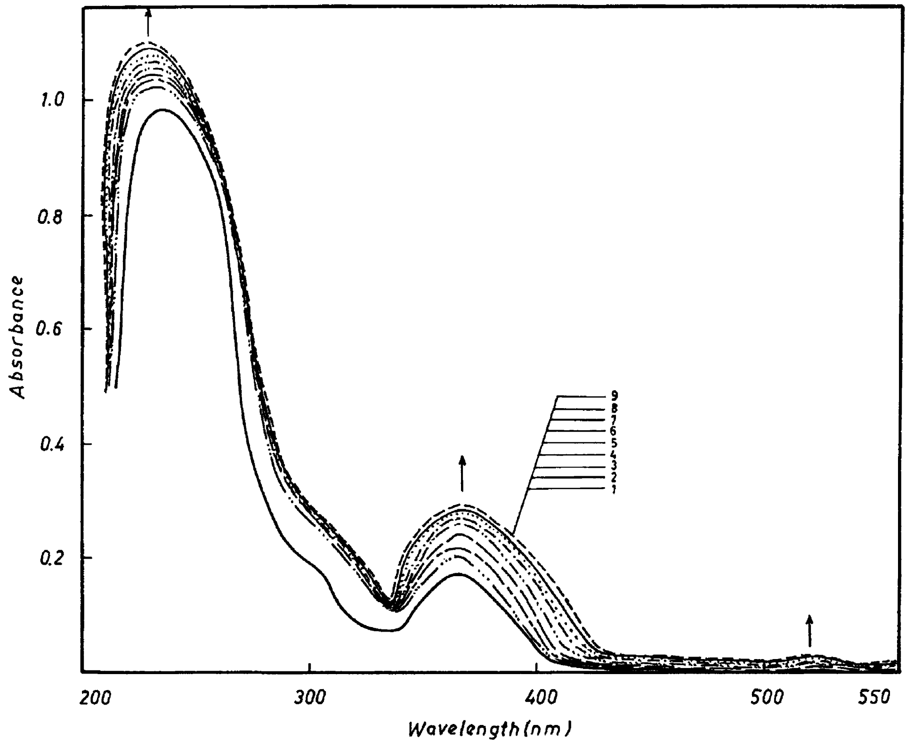

Fig. 7. Electronic absorption spectra of cation $[W(CO)_3(TRZA)I_2]$. Spectral changes at 365 nm accompanying change in irradiation time in chloroform solvent at 289 K. (1) 0, (2) 60, (3) 120, (4) 180, (5) 240, (6) 300 and (7) 360 min.

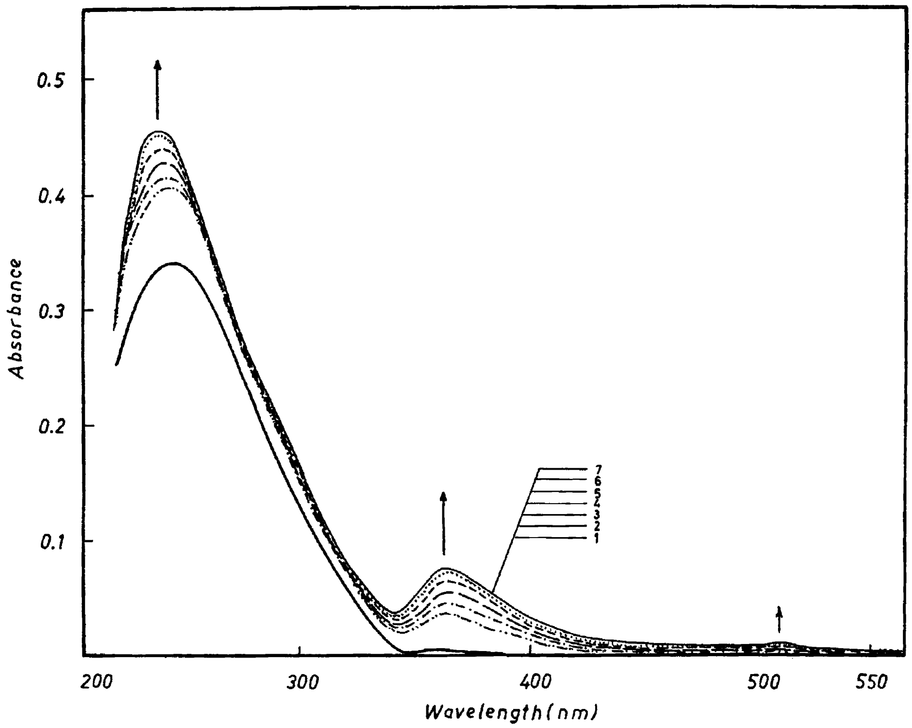

Fig. 8. Electronic absorption spectra of cation $[W(CO)_3(bp)(BIMDA)]^{2+}$. Spectral changes at 365 nm accompanying change in irradiation time in chloroform solvent at 289 K. (1) 0, (2) 60, (3) 120, (4) 180, (5) 240, (6) 300, (7) 360, (8) 420 and (9) 480 min.

Table 4
Specific rate constant (K_d), the quantum yield (Φ_d) of mixed ligand molybdenum and tungsten di- and tri-carbonyl compounds in chloroform solvent "irradiation wavelength 365 nm at 25 °C"[a]

Compound no.	I_0 ($\times 10^{-6}$ Einstein l^{-1} s^{-1})	I_{abs} ($\times 10^{-7}$ Einstein l^{-1} s^{-1})	[Complex] ($\times 10^{-5}$ mol l^{-1})	K_d ($\times 10^{-5}$ s^{-1})	Φ_d ($\times 10^{-4}$)
1	9.135	11.220	2.532	3.8977	8.891
2	9.143	10.689	2.525	4.3746	10.3210
3	9.132	14.053	2.510	4.12222	10.346
4	9.100	10.652	2.500	4.16032	10.494
5	9.433	12.026	2.529	3.46429	8.7611
6	9.100	16.005	2.511	3.31579	8.325
7	8.898	10.652	2.500	3.91104	9.777
8	8.898	10.534	2.525	4.79696	12.112
9	8.879	12.200	2.501	3.7246	9.315
10	8.872	13.356	2.510	3.65397	9.1912

[a] I_0: incidence light intensity, I_{abs}: absorbed light intensity.

3.2. Determination of quantum yield (Φ)

The determination of quantum yield (Φ_d) has been done for each complex after the determination of absorbed light intensity I_{abs} and incidence light intensity I_0 as follows:

$$\begin{aligned} I_{abs} &= I_0(1 - e^{-\varepsilon cl}) \\ &= 9.135 \times 10^{-6}(1 - e^{-(0.05184\times 2.532\times 10^{-5}\times 1)}) \\ &= 11.22 \times 10^{-7}\ \text{Einstein}\ l^{-1}\ s^{-1}\ \text{for complex (1)} \end{aligned} \qquad (3)$$

The quantum yield Φ has been calculated according to Eq. (4):

$$\begin{aligned} \Phi_d &= \frac{\text{rate}}{I_{abs}} = \frac{K[C]}{I_{abs}} = \frac{3.8977 \times 10^{-5} \times 2.532 \times 10^{-5}}{11.22 \times 10^{-7}} \\ &= 8.89 \times 10^{-4}\ \text{for complex (1)} \end{aligned} \qquad (4)$$

The value Φ_d for all mixed ligand metal di- and tri-carbonyl complexes are given in Table 4. The values of Φ for these compounds are in the range (8.3–12.1) × 10^{-4} which are relatively low for such photochemical reactions that may be due to the low intensity of absorption band at 365 nm in these compounds and these results are similar to the other, photodecomposition reactions of carbonyl complexes in homogenous systems [1,19,20], and it is reported to be for a primary process.

3.3. Qualitative analysis of photolysis products "identification"

It is essential to examine the final products of photolysis in order to set up the mechanism; therefore, it has been shown that the final products of the photoreactions undergo a change in color from colorless to pale yellow which gave us the idea to examine the liberated iodine in these products. Starch test shows positive result for all carbonyl compounds, also UV–Vis spectra show a peak at 508 nm indicative of iodine. The following reaction may explain the formation of iodine [21]:

$$2I^- + 4H^+ + O_2 = I_2 + 2H_2O \qquad (5)$$

Infrared (IR) spectra have been recorder for the final photoproducts of these reactions. Fig. 9 shows that there is only two peaks appearing at 925 and 785 cm^{-1} for complex (2), which clearly show that the complex have been photodecomposed to metal oxide MoO_3 and other band for C–Cl group

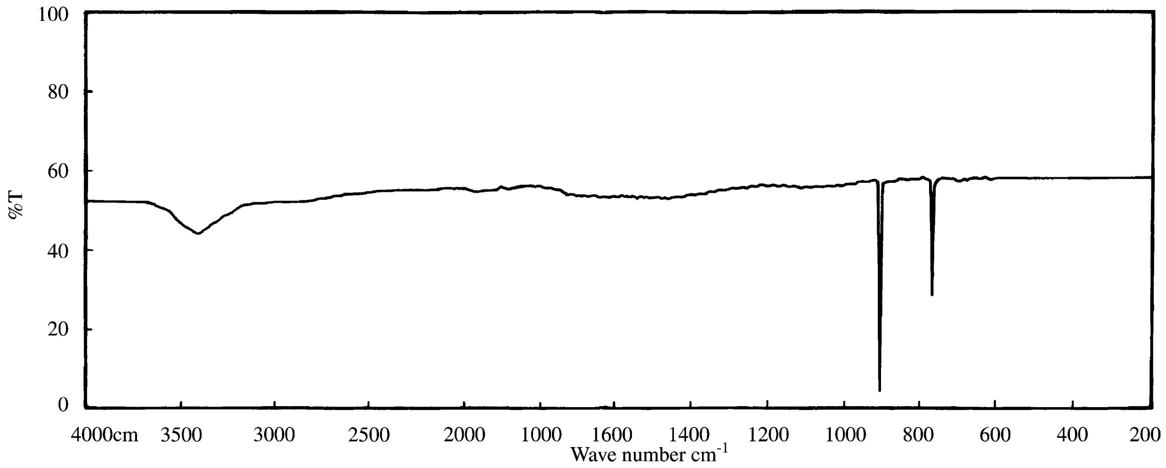

Fig. 9. IR spectrum of cation $[Mo(CO)_3(bipy)(TRZA)]^{2+}$ after prolonged irradiation time in chloroform solvent.

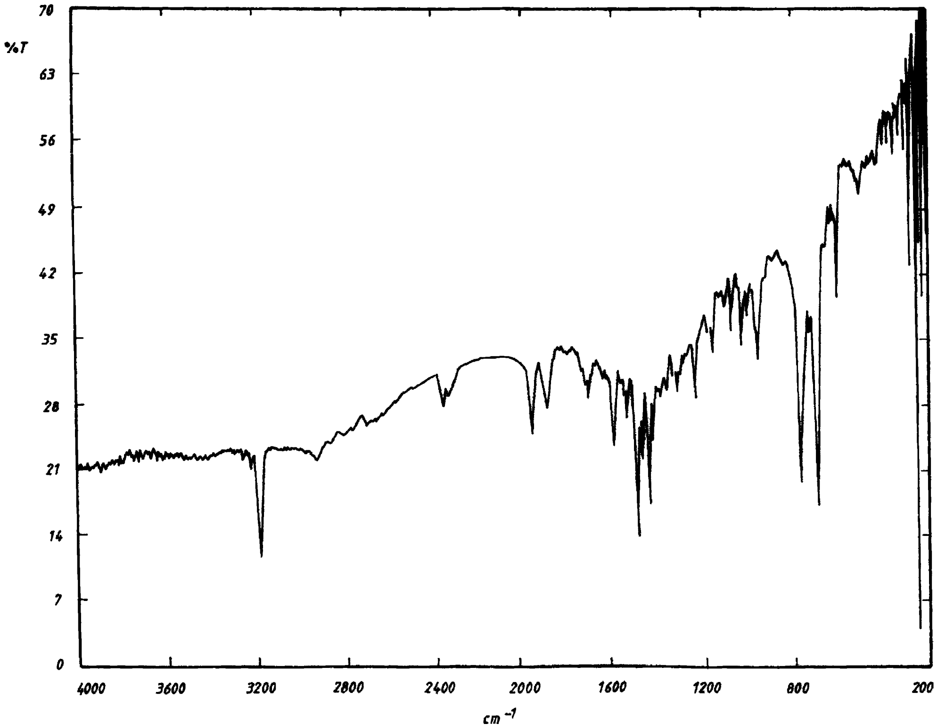

Fig. 10. IR spectrum of cation $[Mo(CO)_3(bipy)(TRZA)]^{2+}$ before photolysis.

of chloroform. The difference between (Fig. 10) before irradiation and (Fig. 9) after irradiation for example (2) shows that there is complete degradation of this complex metal oxide and stable ions via a series of secondary reactions. The analysis of sulfur have been done by testing $SO_4{}^{-2}$ using $BaCl_2$ reagent [22], positive result show the sulfur atom in the complex have been converted finally to the $SO_4{}^{-2}$. Analysis for $NO_3{}^{-}$ have also been done using classical analytical method [22], after separation of interference of iodide in the solution, positive (brow-ring) have been detected depending on the number of nitrogen atom in the complex [18,22].

The analysis of phosphorous have been done also to the final photoproduct by examining the $PO_4{}^{\equiv}$ test using $(NH_4)_3PO_4$ reagent, positive result show the phosphorous atom in the complex has been converted finally to $PO_4{}^{\equiv}$.

The acidity of the final photoproduct also has been done by measuring pH during the photolysis which was increased with time of irradiation, the initial acidity was at pH 5.95 and the final was at 2.23.

Finally, the measurement of photoproduct of the photolysis in our closed photocell shows that evaluation of CO have been detected beside oxygen by measuring the gas flow during the irradiation time by analysis of gas sample using gas chromatography.

3.4. Determination of the reaction mechanism

The photodegradation of these complexes take place with UV light without a catalyst and when there is oxygen gas present, the following equation represents the reaction taking place [18,23]:

$$[\text{Complex}]I_2 \xrightarrow[O_2]{h\nu} [\text{complex-}O_2{}^{\bullet}]^{*}I_2$$

With the very low primary quantum number shown above and identification of the final photoproducts as the metal oxide and iodine colouration indicate that the excited state (organometallic complex) undergoes internal rearrangement to the final oxide [24] and other ions as shown:

$$[\text{Complex-}O_2{}^{\bullet}]^{*}I_2 \rightarrow M_XO_Y + I_2 + CO + \text{stable ions}$$

Similar research work has been done on the photocatalytic carbonyl reducing system [18,25], and hydrogen generation from $Cr(OX)_3H_2O$ using ferrous ion in homogenous system [26], formation of new stable small molecules or stable ions, as carbonyl metal complexes, or semiconductor such as TiO_2, ZnO, ... can behave as sensitizer in the presence of oxygen or it may decomposed through photo-oxidation degradation of final stable molecules or ions [6]:

$$H-C\equiv C-H \xrightarrow[Mo_2S_4(S_2C_2H_4)_2{}^{-2}]{TiO_2\,/\,O_2} {>}C=C{<} + CH_3CH_3 \qquad (6)$$

These types of reactions have an application in environmental degradation or mineralization of polluted water [6,18,27]:

$$\text{Pollution molecule} \xrightarrow[TiO_2/O_2]{h\nu} \text{stable ions or molecule} \qquad (7)$$

All these final photoreactions have been suggested without proposing the exact primary process.

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