Photodecomposition of Molybdenum and Tungsten Carbonyl Complexes

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Abstract: The photodecomposition of four different colored organometallic molybdenum and tungsten carbonyl complexes, *i.e.* $[\text{Mo}(\text{CO})_5\text{L}_A]$ (complex I), $[(\text{Mo}(\text{CO})_3(\text{bipy}))_2\text{L}_B]$ (complex II), $[(\text{W}(\text{CO})_3(\text{tmen}))_2\text{L}_B]$ (complex III) and $[\text{Mo}(\text{CO})_2\text{L}_C]_2$ (complex IV) where L_A 2-phenyl-1,3-indandione bis(2-methyl anilines), L_B 2-phenyl-1,3-indandione bis (4-hydroxy anilines) and L_C bis (2-hydroxy-benzaldehyde) benzidine ion have been performed at 365 nm in chloroform at 25 °C under oxygen atmosphere. The absorbance spectrum of these complexes has been recorded with the time of irradiation in order to examine the kinetics of photodecomposition. The rate of the photodecomposition process was investigated and the relative values of the rate constants of dissociation (K_d) for the first-order reaction are tabulated. The apparent rate constant of photodecomposition was found to be $(8.33\text{--}11.50) \times 10^{-5} \text{ s}^{-1}$.

Keyword: Photodecomposition, Molybdenum, Tungsten, Carbonyl complexes, Chemical decomposition, Photochemical reaction.

Introduction

There are many applications of metal carbonyl complexes, such as, photochemical conversion reactions for hydrogen production, photo oxidation of complexes, photo initiator in polymerization processes, homogeneous and heterogeneous catalysts and as infrared markers for hormonal steroids in biological processes¹⁻⁴. Lees⁵ reviewed the employments of several organometallic complexes as luminescence probes to monitor industrially important thermal and photochemical polymerization reactions. Many authors⁶ reported the important roles of highly unsaturated transition-metal carbonyl complexes role in different processes such as homogeneous catalysis and single-photon and multiphoton decomposition of organometallic.

In the present work, the photolysis of four different colored organometallic molybdenum and tungsten carbonyl complexes in chloroform was initiated by irradiation with UV light at 365 nm. The degradation percentage was investigated spectrophotometrically by measuring

the maximum absorption at 493.5 nm for complex I, 483 nm for II, 482 nm for III and 506 nm for IV. These wavelengths were selected to match the absorption maxima in the electronic spectra of the complexes.

Experimental

[Mo(CO)₅]₂L_A] (complex I), [(Mo(CO)₃(bipy))₂L_B], (complex II), [(W(CO)₃(tmen))₂L_B] (complex III) and [Mo(CO)₂L_C]₂ (complex IV) were prepared and identified before⁷. The instrument used in photodecomposition of complexes was described before⁸. In all experiments 30 cm³ of one of the four complexes dissolved in chloroform (1×10⁻⁴ M) was placed in the photoreaction cell. To ensure an equally exposure of all solution to UV irradiation, continues stirring was done with a magnetic stirrer. The cell contains side arms for passing air and for water circulation around the cell in order to keep temperature of the reaction at a desired value.

The cell was fitted with ultraviolet radiation from a low pressure mercury lamp, type TQ150Z2. Periodically 3 cm³ of irradiated samples were withdrawn by small syringe and the absorbance was measured using U.V. visible spectrophotometer (Centra 5 -GBC-Austral) and then returned back to the reaction cell. The absorbance at a given time compared with a calibration curve. The calibrating plot obtained by using known concentrations of each complex. FTIR spectra were obtained with FTIR-8400-Shimadzu, Single Beam path laser. All experiments were performed under an atmosphere of oxygen.

Results and Discussion

Table 1 show the values of molar absorption extinction coefficients of the four complexes which ranges between 9412-12727 dm³ cm⁻¹ mole⁻¹. The high values related to nature of electronic transition occur within the complex⁹⁻¹⁰. These electronic transitions include (n→π*), (π→π*) metal ligand charge transfer and ligand metal charge transfer.

Table 1. Molar absorption extinction coefficients of complexes.

Complex	$\epsilon / \text{mol}^{-1} \text{L.cm}^{-1}$
I	10714
II	12727
III	12176
I V	9412

The rate constants of dissociation (K_d) for the photodecomposition of the four complexes were calculated by using the following equation:

$$\ln A_t - A_\infty / A_0 - A_\infty = -K_d t \quad (1)$$

Where A_0 represents the absorbance of the complex at time zero, A_t the absorbance at t time and A_∞ the absorbance after irradiation time of seven hours. A plot of $\ln A_t - A_\infty / A_0 - A_\infty$ against time, as shown in Figure 1, showed that the assumption of an apparent first order reaction was valid for all complexes, as can be seen by the linear regressions ($R^2 > 0.9992$).

The values of the rate constants of dissociation (K_d) for the four complexes, which ranges between 8.33×10^{-3} - 11.50×10^{-3} , were obtained from equation 1 and are summarized in Table 2.

Table 2. Rate constants of dissociation for complexes

Complex	$K_d \text{ s}^{-1}$
I	11.50×10^{-3}
II	9.00×10^{-3}
III	9.50×10^{-3}
I V	8.33×10^{-3}

Figure 1. Plot of $\ln A_t - A_\infty / A_0 - A_\infty$ against time.

Figure 2. IR spectral changes of complex I; (A- Before irradiation B- After irradiation).

Figure 2 shows the IR-spectra of complex I before and after photodecomposition. The $\nu(\text{CO})$ peaks are clearly discernible in this spectrum (before photodecomposition) at 1870, 1898, and 1970 cm^{-1} . Apparently photodecomposition of this complex leads to disappearance of these bands relating to the formation of CO and simultaneously to appearing a new intensive band 938 cm^{-1} which points out to the formation of Mo=O

These findings are in good agreements with previous findings¹¹⁻¹². Mishchenko *et al*¹³ reported that photodecomposition of styrene, stilbene, and 1,4-diphenylbuta-1,3-diene tricarbonyl chromium complexes in hydrocarbon solvents yield of CO was 1 mol per mole of the converted chromium complex. Barnett *et al*¹⁴ observed the formation of CO when they applied FT-Raman spectroscopy to the study the photodecomposition of selected organometallic complexes. These data proved that $[\text{Mo}(\text{CO})_5)_2\text{L}_\text{A}]$ (complex I) photodecomposition follows the following equation:

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