

Photoactivation of Carbonyl Sulphide in Presence of Platinum Metal Ions & Their Complexes

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The photolytic reactions of carbonyl sulphide with ruthenium (II), ruthenium (III), rhodium (I) complexes and with $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and PdCl_2 in the presence of excess of PPh_3 and AsPh_3 have been investigated. The reaction products have been characterised by elemental analyses, IR spectra and other physicochemical data. In most of the cases the photoactivated reactions show significant differences when compared product-wise with thermally activated reactions.

IN recent years various photolytic processes like photoisomerisation, photocatalysis, photooxidation, photosubstitution etc. have been reported in the literature¹⁻⁶. It is well known that COS can be photolysed by the UV radiations to give CO and S. It will be an interesting study if the photolysis of COS is carried out in the presence of some transition metal ions and their complexes which may yield carbonyl, sulphide, or/and other types of reaction products, depending on the nature of the metal ion and the complexes. Since we have already reported⁷⁻¹⁰ our findings on the thermal reactions of COS with Rh, Pd and Ru complexes in presence of PPh_3 , AsPh_3 or SbPh_3 in CH_2Cl_2 and methanol solutions, it is considered interesting to compare the nature of products in the thermal and photolytic reactions of COS. In this paper we wish to report the photolysis of COS in the presence of PPh_3 or AsPh_3 and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, PdCl_2 , $\text{RuCl}_2(\text{PPh}_3)_3$, $\text{RuCl}_3(\text{AsPh}_3)_3$, $\text{RuH}_2(\text{PPh}_3)_3$ and $\text{RhCl}(\text{PPh}_3)_3$. The products have been characterised by elemental analyses, IR spectra, magnetic data, conductivity and molecular weight measurements.

Materials and Methods

All the reagents used were chemically pure. $\text{RuCl}_2(\text{PPh}_3)_3$ (ref. 10), $\text{RuCl}_3(\text{AsPh}_3)_3$ (ref. 11), $\text{RuH}_2(\text{PPh}_3)_3$ (ref. 12), $\text{RhCl}(\text{PPh}_3)_3$ (ref. 13) and saturated solution of COS¹⁴ in methanol were prepared by standard methods. In every reaction a fresh solution of COS was used.

General irradiation procedure — Photoactivations were carried out, in general, at 250 nm using a 450 watt Hanovia high pressure Hg lamp equipped with water filter. Solutions (to be photoactivated) were taken in an immersion type photoreactor (500 ml capacity). The solution and the lamp were separated by a cooling quartz jacket ($\sim 20^\circ\text{C}$) to avoid undesirable heating effect. A very dilute solution of the reactants were always used to ensure sufficient photoactivation. Photoactivations were

indicated by a colour change of the solution or suspension or formation of a precipitate.

Some of the photoactivations were carried out at 253.7 nm in a Rayonet's Srinivasan-Griffin photochemical reactor. However, in this jacket-type photoreactor solution was kept for a longer time to ensure complete photoactivation due to the low intensity of the irradiation used.

(1) *Photoactivation of COS in the presence of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and PPh_3* — A methanolic solution (50 ml) of COS was added to a solution of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (0.02 g) and PPh_3 (0.12 g) in methanol (450 ml) and the solution irradiated for 1 hr with stirring. The green solution thus formed was filtered and the filtrate concentrated in a flash evaporator at 75°C under reduced pressure to 3–4 ml. Ether was added to it in large excess whereby a greenish black compound was precipitated which was filtered, washed with ether and purified by dissolving in CH_2Cl_2 and reprecipitation with ether.

(2) *Photoactivation of COS in the presence of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and AsPh_3* — The reaction mixture containing $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (0.02 g) and AsPh_3 (0.12 g) in methanol (450 ml) and a solution (50 ml) of COS in methanol was irradiated for 0.5 hr. A reddish brown solution thus obtained was concentrated in a flash evaporator (as stated earlier) whereby a reddish brown crystalline compound was precipitated. It was filtered, washed with ether, and recrystallised from CH_2Cl_2 and ether.

(3) *Photoactivation of COS in the presence of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and PPh_3* — The reaction mixture and irradiation procedure was the same as in (1), except that $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was used in place of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and time of irradiation was 15 min. The yellow crystalline compound obtained was filtered, washed with methanol and ether and dried *in vacuo*.

(4) *Photoactivation of COS in the presence of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and AsPh_3* — The reaction mixture and procedure was the same as in (3), except that the time of irradiation was 30 min. and AsPh_3 was used instead of PPh_3 . The red crystalline compound formed

was filtered, washed with methanol and ether and dried *in vacuo*.

(5) *Photoactivation of COS in the presence of PdCl₂ and PPh₃* — PdCl₂ (0.02 g) was dissolved by heating it in dimethyl sulphoxide (15 ml) and cooled to room temperature. A methanolic solution (50 ml) was added to it followed by the addition of PPh₃ (0.12 g) and sufficient methanol to make the total volume to about 500 ml. The mixture was irradiated with stirring for 30 min. The yellow crystalline compound formed was filtered, washed with methanol and ether and dried *in vacuo*. This was found to be a mixture of two compounds, Pd(PPh₃)₂Cl₂ and Pd(PPh₃)₂ COS which were separated by column chromatography and their identities established by direct comparison (m.p., m. m. p., IR co-IR) with authentic samples.

(6) *Photoactivation of COS in the presence of PdCl₂ and AsPh₃* — The reaction mixture and procedure was the same as that given in (5) except that AsPh₃ was used instead of PPh₃. The bright yellow crystalline compound thus obtained was a mixture of Pd(AsPh₃)₂Cl₂ and Pd(AsPh₃)₂ COS which were separated by column chromatography their identities established by direct comparison with authentic samples.

(7) *Photoactivation of COS in the presence of RuCl₃ (AsPh₃)₃ and AsPh₃* — RuCl₃ (AsPh₃)₃ (0.2 g), AsPh₃ (0.8g) and a methanolic solution (50 ml) of COS were added in enough CH₂Cl₂ in order to make a clear solution. It was taken in the photo-reactor and the volume was made upto 500 ml with methanol. This was irradiated for 30 min with stirring whereby a brownish precipitate was obtained which was filtered, washed with alcohol and ether and dried *in vacuo*.

The remaining filtrate was concentrated in a flash evaporator of 75° under reduced pressure and the oily mass thus obtained extracted with minimum volume of CH₂Cl₂. Excess ether was added to it whereby a greenish black precipitate was obtained. The compound was filtered, washed with ether and purified by dissolving in CH₂Cl₂ and reprecipitating with ether and dried *in vacuo*.

(8) *Photoactivation of COS in the presence of RuH₂(PPh₃)₃ and PPh₃* — The reaction mixture and the procedure were the same as in (7), using RuH₂(PPh₃)₃ and PPh₃ as reactants. After irradiation a black compound was obtained which was filtered, washed with methanol and ether and dried *in vacuo*. (The percentage of yield of the complex was increased by concentrating the mother liquor under reduced pressure). The product was purified by dissolving it in CH₂Cl₂ and reprecipitating with ether.

(9) *Photoactivation of COS in the presence of RhCl(PPh₃)₃ and PPh₃* — A methanolic solution (50 ml) of COS was added to a solution of RhCl(PPh₃)₃ (0.2 g) and PPh₃ (0.2 g) in CH₂Cl₂ (20 ml) and the volume made upto 500 ml with methanol. The mixture was irradiated for 30 min with stirring whereby a yellow crystalline complex was obtained. This was filtered, washed with methanol and ether and dried *in vacuo*.

The remaining reddish brown filtrate on concen-

tration in a flash evaporator at 75° under reduced pressure, yielded a deep brown solution which on cooling gave a brown compound. It was filtered, washed with ether and purified by dissolving it in CH₂Cl₂ and reprecipitating with ether. It was dried *in vacuo*.

Results and Discussion

All the compounds reported here were purified by recrystallization from suitable solvents. The analytical data are recorded in Table 1, alongwith their IR data. The purity of the complexes were further tested by preparing them a number of times and analysing them.

The oxidation states of the metal ions and the probable geometries of the complexes have been arrived at by measuring the magnetic properties and molecular weights. The known compounds have been characterized by direct comparison with authentic samples.

Photolysis of COS in solution at room temperature with 220 < λ < 310 nm resulted in the rupture of C-S bond with the formation of activated CO and the sulphur atom in ¹D (~ 74%) and ³P (~26%) states¹⁶. There is a possibility of formation of carbonyl and/sulphide complex if photolytic decomposition of COS is carried in the presence of metal ions or its complexes. Under similar conditions the thermal decomposition products may be complicated, but, if the metal complexes capable of forming h²-COS complex along with thiophilic ligands like PPh₃ are present, COS molecule can be activated to carbonylate the metal ion and to form the triphenylphosphine sulphide which may substitute the ligand on the metal ion. Similar results of the formation of SPPPh₃ and subsequent replacement of PPh₃ from the metal complex is also a possibility in photolytic reactions.

The photolysis reaction of COS with PdCl₂ in presence of MPh₃ (M = P or As) gave Pd(MPh₃)₂ COS, a complex also identified in the thermochemical reaction⁹, and a known compound Pd(MPh₃)₂Cl₂. The preferential combination of Pd with COS over CO may be because of low tendency of Pd to form carbonyls.

Similar to the thermal reactions^{8,10}, photolysis of COS with RuCl₃.xH₂O and RhCl₃.3H₂O in the presence of PPh₃ resulted in the formation of carbonyls of Ru²⁺ and Rh¹⁺, and SPPPh₃ which besides being detected in the filtrate combined with rutheniumcarbonyl to give [RuCl₂(CO)(SPPPh₃)₂]. The rate of photolytic reactions are relatively faster than thermochemical reactions and more so in the presence of Ru compounds.

The photolysis of COS in the presence of RhCl(PPh₃)₃ and PPh₃ gave predominantly the known compound, Rh(CO)Cl(PPh₃)₂ and SPPPh₃ which being excess in solution replaced PPh₃ from unprecipitated Rh(CO)Cl(PPh₃)₂ to form Rh(CO)Cl(SPPPh₃)₂ in low yield. However, the yield of the latter compound, in contrast to that obtained in the thermal reaction was lower as compared to Rh(CO)Cl(PPh₃)₂. It is suggested that in photochemical reaction the chemically active species, RhCl(PPh₃)₂ reacts

TABLE 1—ANALYTICAL & STRUCTURAL DATA OF THE COMPLEXES

Formula (mol. wt)	m.p. (°C)	Found (calc.) (%)					Major IR bands other than MPh ₃ (in cm ⁻¹) (M = P, As)
		C	H	S	Cl	Pd	
Rh(CO)Cl(PPh ₃) ₂ (735)	200	64.6 (64.3)	4.7 (4.3)	—	5.0 (5.1)	—	ν(CO), 1960; δRh-CO, 575
[RhCl(OAsPh ₃)(SAsPh ₃) ₂]	205	53.6 (54.1)	3.6 (3.7)	4.6 (4.0)	4.7 (4.4)	—	ν(As=O), 880; ν(As=S), 465
[Ru(CO)(SPPH ₃)Cl ₂] ₂	300	45.9 (46.1)	3.0 (3.0)	5.9 (6.5)	14.2 (14.4)	—	ν(CO), 1965
[RuCl ₂ (SAsPh ₃)(AsPh ₃) ₂]	220	52.6 (52.9)	3.7 (3.7)	4.0 (3.9)	9.1 (8.7)	—	No extra band
Pd(PPh ₃) ₂ COS(716)	196	63.8 (64.3)	4.8 (4.4)	4.8 (4.6)	—	15.1 (15.4)	ν(C=O), 1642; ν(C-O), 1180; ν(C=S), 1120; ν(C-O), 850; ν(C-S), 810.
Pd(AsPh ₃) ₂ COS(762)	203	56.9 (57.0)	3.8 (3.9)	4.3 (4.1)	—	12.9 (13.6)	ν(C=O), 1640; ν(C-O), 1185; ν(C=S), 1128; ν(C-O), 845 ν(C-S), 815.
Rh(CO)Cl(SPPH ₃) ₂	215	58.5 (58.8)	4.0 (3.9)	8.2 (8.5)	4.3 (4.7)	—	ν(CO), 1946; ν(P=S), 550
[Ru(CO)Cl ₂ (AsPh ₃) ₂](928)	212	45.3 (45.1)	2.7 (2.9)	—	13.8 (14.0)	—	ν(CO), 1958
[RuCl ₂ (OAsPh ₃)(SAsPh ₃) ₂]	145	52.4 (51.9)	3.4 (3.6)	3.6 (3.8)	8.4 (8.5)	—	ν(As=O) 880; ν(As=S), 500.
Ru ₂ (PPh ₃) ₂ (CO) ₄ S ₂ (847)	175	53.6 (53.2)	3.4 (3.3)	7.4 (7.1)	—	—	ν(CO), 1955

*Chloride and sulphur were estimated by standard method (ref. 159) after decomposing the complexes with aqua regia or NaOH + NaNO₃ mixture.

with activated CO generated by primary photo-process while in thermal reaction PPh₃ pulls out sulphur from the first formed h²-COS Rh complex to form SPPH₃ which then competes with PPh₃ to form either Rh(CO)Cl(PPh₃)₂ or Rh(CO)Cl(SPPH₃)₂.

Photolytic reactions of COS in the presence of RuCl₃.xH₂O or RhCl₃.3H₂O and AsPh₃ yielded products similar to these obtained in the thermal reaction. However, ruthenium gave mainly [RuCl₂(SAsPh₃)(AsPh₃)₂] while rhodium yielded [Rh(OAsPh₃)(SAsPh₃)Cl]₂. Oxidation of the ligated AsPh₃ occurred presumably by atmospheric oxygen¹⁷. The latter compound showed an intense IR band around 1265 cm⁻¹ which could also be assigned to ν(C=S). But the photo-dissociation of COS leading to CS group is highly improbable¹⁸. Therefore, the possibility of the formation of C=S is ruled out, and the band at 1265 cm⁻¹ could be a shifted band of AsPh₃ or its derivatives.

Photolysis of COS in the presence of RuCl₃(AsPh₃)₃ yielded first a precipitate characterised as [Ru(CO)Cl₂(AsPh₃)₂]. Another complex, [RuCl₂(OAsPh₃)(SAsPh₃)₂] was isolated from the filtrate. Similar photolytic reactions involving RuCl₂(PPh₃)₃ yielded a mixture of SPPH₃ complexes which could not be separated in pure state.

Reactions of RuH₂(PPh₃)₃ with COS under photolytic conditions yielded products similar to those in the thermal reaction.

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