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Reductive Nitrosation of Molybdenum and Tungsten Halides. III.* Intramolecular Redox Reactions of Molybdenum and Tungsten Halo Nitrosyl Complexes**

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Thermally initiated exothermic intramolecular redox reactions of $[M(NO)_2Cl_2]_n$ and $M(NO)_2Cl_2L_2$ (where M = Mo or W; L = PPh_3AsPh_3 or $OPPh_3$) type complexes were observed at definite temperatures. In these reactions the coordinated NO oxidizes M or L and N_2O or N_2 containing gases are formed. Thermal analysis was found to be a reliable supplementary method to differentiate between phosphine and phosphine oxide substituted halo nitrosyl complexes.

Introduction

Some reactions of $MoCl_5$ and WCl_6 with NO have been reported recently.[1–5] Since in these reactions NO is simultaneously acting as a reducing and coordinating agent, this sequence of reactions has been termed reductive nitrosation.[3]

The products were usually identified by their IR spectra and elemental analysis. The latter has been found to be satisfactory for the halo metal nitrosyls with respect to the metal, the halogen and the phosphorus, but the nitrogen found after digestion[6] by the Kjeldahl method never reached the calculated values.

Results and Discussion

The above observations made it probable that some reactions might occur under digestion conditions in which the nitrogen content of the compounds is transformed into nitrogen compounds inert against the common reducing or oxidizing agents. To justify this supposition $Mo(NO)_2Cl_2(PPh_3)_2$ was heated in a current of CO_2 and the gases evolved were collected in an azometer over an aqueous KOH solution. The model compound was fairly stable still 200° C, when an explosion-like decomposition started accompanied by gas evolution. According to GLC analysis this gas consisted mainly of N_2 besides some N_2O and NO. The N content, based on the quantity and composition of gases evolved was in good agreement with that calculated for $Mo(NO)_2Cl_2(PPh_3)_2$ (N found: 3.75%; N calcd.: 3.8%).

This result essentially confirmed the starting assumption that thermally initiated redox reactions inside of halo nitrosyl complexes may lead to the transformation of coordinated NO into N_2 and N_2O. In order to extend this statement to other complexes the thermal decomposition of several Mo and W halo nitrosyl derivatives was studied by the method above (Table I).

The decomposition of the unsubstituted $[M(NO)_2Cl_2]_n$ (M = Mo or W) complexes was especially vigorous and accompanied by acculting light. In these reactions the oxygen atoms of the NO ligands were partly transfered to the central atom forming oxichlorides besides some metal. The stoichiometry of these reactions may be described by the following equation:

$$4[M(NO)_2Cl_2]_n \xrightarrow[t]{\Delta} nMOCl_4 + 2nMO_2Cl_2 + nM + 3n\,N_2O + nN_2 \quad (1)$$

(where M = Mo and t = 340° C, or M = W and t = 350° C).

The oxihalides sublimed into the cooler part of the reaction vessel in two separate layers from where they were isolated but 25–27 per cent of the metal content was found in the vessel as a black free metal residue. This means that at least 25 per cent of the metal content of $MoCl_5$ and WCl_6 was reduced to free metal by reductive nitrosation and subsequent thermolysis, a series of reactions in which NO is the only reducing agent.

The decomposition temperatures of $M(NO)_2Cl_2(PPh_3)_2$ type complexes were much lower and the majority of the gaseous products was N_2. The molybdenum and tungsten compounds were stable only up to 190 and 265° C, respectively, and the coordinated NO oxidized not the central atom but the phosphine ligands:

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* For part II. see ref. 4.

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TABLE I. Thermally Initiated Exothermic Intramolecular Redox Reactions of Molybdenum and Tungsten Halo Nitrosyl Complexes.

Substance	Initial Temperature of Oxygen Transition, °C		Main Component of Gas Evolved
	from N to P (As)	from N to M	
$[Mo(NO)_2Cl_2]_n$		340	N_2O
$[W(NO)_2Cl_2]_n$		350	N_2O
$Mo(NO)_2Cl_2(PPh_3)_2$	190		N_2
$Mo(NO)_2Cl_2(AsPh_3)_2$	280		N_2
$W(NO)_2Cl_2(PPh_3)_2$	265		N_2
$Mo(NO)_2Cl_2(OPPh_3)_2$		300	N_2O
$Mo(NO)_2Cl_2(OPPh_3)_2 \cdot 2C_6H_6$		300	N_2O
$W(NO)_2Cl_2(OPPh_3)_2$		310	N_2O

$$M(NO)_2Cl_2(PPh_3)_2 \xrightarrow{\Delta} [MCl_2(OPPh_3)_2] + N_2 \quad (2)$$

These M^{II} halide complexes could not be isolated since their decomposition started just after the N_2 evolution. Their formation is indicated by the TG curves (Fig. 1a).

Since arsine ligands are more stable to oxidation than phosphines, the redox reaction in the case of $Mo(NO)_2Cl_2(AsPh_3)_2$ started only at 280 °C.

The temperatures necessary for the initiation of the decomposition of $M(NO)_2Cl_2(OPPh_3)_2$ type complexes were higher still and approached those of the unsubstituted halo nitrosyl complexes: 300 °C for Mo and 310 °C for W derivatives. In these reactions the central metal atoms were oxidized and the gas evolved was mostly N_2O:

$$M(NO)_2Cl_2(PPh_3O)_2 \xrightarrow{\Delta} [MOCl_2(OPPh_3)_2] + N_2O \quad (3)$$

These phosphine oxide substituted thermolysis products seem to be slightly more stable then those formed in reaction (2) but were still too unstable at about 300 °C to be isolated, and decomposed rapidly losing the two phosphine oxide molecules.

Owing to the large difference between the decomposition temperature of phosphine and phosphine oxide substituted derivatives, thermoanalysis has been found to be a reliable method for the differentiation between phosphine and phosphine oxide substituted molybdenum and tungsten halo nitrosyl complexes.

$Mo(NO)_2Cl_2(OPPh_3)_2 \cdot 2C_6H_6$ (ν_{NO} = 1662s, 1784s) lost its benzene content in one endothermic step:

$$Mo(NO)_2Cl_2(OPPh_3)_2 \cdot 2C_6H_6 \xrightarrow[100°C]{\Delta} Mo(NO)_2Cl_2(OPPh_3)_2 + 2C_6H_6 \quad (4)$$

The product is composed of two isomers. Since both were stable between 100 and 300 °C they could be

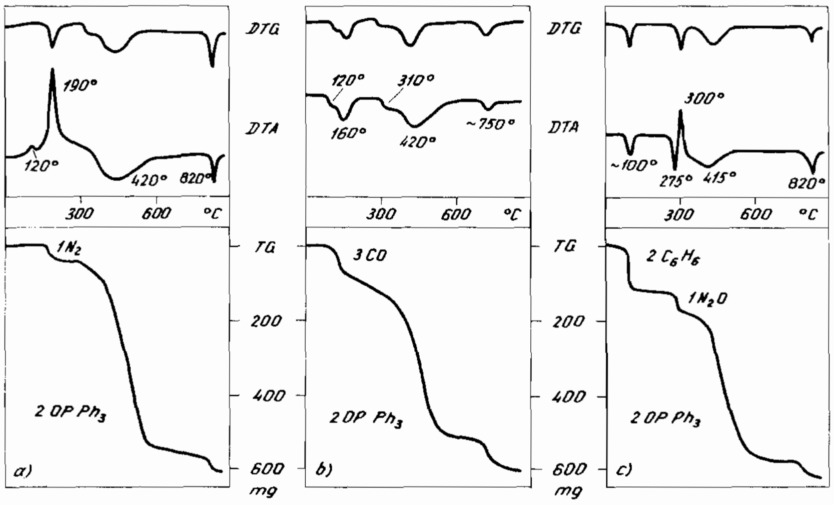

Figure 1. TG, DTG and DTA curves of $Mo(NO)_2Cl_2(PPh_3)_2$ (a), $Mo(CO)_3Cl_2(OPPh_3)_2$ (b) and $Mo(NO)_2Cl_2(OPPh_3)_2 \cdot 2C_6H_6$ (c).

TABLE II. TG Data of $M(NO)_2Cl_2L_2$ Type Complexes (M = Mo or W; L = PPh_3, $AsPh_3$ or $OPPh_3$).

Substance	Weight Loss "A", mg/mmol	Leaving Group	Weight Loss "B", mg/mmol	Leaving Group
$Mo(NO)_2Cl_2(PPh_3)_2$	28.8	N_2	555.8	$OPPh_3$
$W(NO)_2Cl_2(PPh_3)_2$	28.5	N_2	546.1	$OPPh_3$
$Mo(NO)_2Cl_2(AsPh_3)_2$	27.9	N_2	644.1	$OAsPh_3$
$Mo(NO)_2Cl_2(OPPh_3)_2$	44.0	N_2O	556.7	$OPPh_3$
$W(NO)_2Cl_2(OPPh_3)_2$	46.4	N_2O	523.6	$OPPh_3$

easily isolated as a mixture (ν_{NO} = 1656s, br, 1773 m, 1782 m). On further heating the decomposition of this mixture was identical with that of $Mo(NO)_2Cl_2$ $(OPPh_3)_2$ (Fig. 1c) prepared in CH_2Cl_2.

Apart from the loss of solvates the decomposition of all $M(NO)_2Cl_2L_2$ complexes investigated followed nearly the same pattern including two main steps. The first exothermic step corresponded to the evolution of nitrogen containing gases (weight loss "A", Table II) and the formation of an unstable $OPPh_3$ or $OAsPh_3$ substituted chloride or oxichloride intermediate. This stage is followed by an endothermic step corresponding to an approximately stoichiometric loss of two $OPPh_3$ or $OAsPh_3$ ligands (weight loss "B", Table II). Final residues of pyrolysis in these cases have not yet been identified.

The thermal behaviour of complexes prepared by either Johnson's method[7,8] or by reductive nitrosation was identical. The rate and H of the redox reactions increased in the order of phosphine oxide-, arsine-, phosphine-substituted, unsubstituted halo nitrosyl complexes.

To study the thermal behaviour of the intermediates and the possibility of oxygen transfer from phosphorus to the metal atom $W(CO)_2Cl_2(OPPh_3)_2$ and Mo $(CO)_3Cl_2(OPPh_3)_2$ complexes were prepared[9] to serve as models with similar formal or isoelectronic structure. Their decomposition was totally endothermic and followed the same pattern. After the loss of carbon monoxide (at 160°C) the TG curves gave no horizontal weight level and the decomposition of the intermediate were nearly identical with those of reaction (2) (Fig. 1b). $W(CO)_2Cl_2(OPPh_3)_2$ was the one of two carbonyl compounds which decomposed more clearly:

$$W(CO)_2Cl_2(OPPh_3)_2 \xrightarrow[160^\circ C]{\Delta} WCl_2(OPPh_3)_2 + 2CO \qquad (5)$$

Since the decomposition in this case was slow between 160°C and 300°C the isolation of WCl_2 $OPPh_3)_2$ might be attempted.

Experimental

All manipulations were carried out under argon or CO_2. Dry ice was used as a CO_2 source. The carrier gas was purified from tracesat N_2 and O_2 as usual.[11] The molybdenum and tungsten halo nitrosyl complexes were prepared both by reductive[3–5] and oxidative[7,8] nitrosation as described in the literature.

The molybdenum and tungsten content of the starting materials and the residues was determined after digestion[6] in the form of $MO_2(C_9H_6NO)_2$ (M = Mo or W) type oxinates.[10]

TG and DTA analyses were made using a MOM G-425 type derivatograph at a heating rate 10°C/min. The weight of samples was about 0.5–1 mmol depending on the weight loss expected.

The quantities of N_2O or N_2 and $OAsPh_3$ or $OPPh_3$ formed as calculated from the TG curves were stoichiometric in the case of molybdenum compounds, but in the case of tungsten derivatives the accuracy was not higher than 95% (Table II).

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