Inorganica Chimica Acta, *170* (1990) 53–57

Dissociation of Solvent Molecules from $Mo_2O_3I_2(dtc)_2(solv)_2$ in Solutions of Non-coordinating Solvents

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(Received September 6, 1989)

Abstract

$Mo_2O_3I_2(dtc)_2(THF)_2$ reacts with solvents in various ways depending on their coordinating ability. With weakly coordinating solvents the coordinatively unsaturated $Mo_2O_3I_2(dtc)_2$ results because the THF molecules have been removed. With moderately coordinating solvents the THF is replaced by solvent molecules resulting in $Mo_2O_3I_2(dtc)_2(solv)_2$. However, NMR and electronic absorption studies indicate that in CH_2Cl_2 and $CHCl_3$ solution the coordinated solvent molecules from the $Mo_2O_3I_2(dtc)_2(solv)_2$ species are dissociated. With the strongly coordinating solvent pyridine a complex results which has no Mo=O bonds.

Introduction

The ability of oxo–molybdenum species to catalyze atom transfer reactions has recently become apparent. The bulk of reports, to date, have been on catalysis based on interconversion of MoO_2^{2+} and MoO^{2+} complexes [1]. Oxo-bridged Mo(V) species which contain the $Mo_2O_3^{4+}$ core have been considered to be unreactive to oxygen atom transfer reactions [2]. Recently, however, two types of $Mo_2O_3^{4+}$ complexes have been reported which do take part in such reactions. These are the tridentate Schiff base complexes, $Mo_2O_3L_2(solv)_2$, reported by Holm *et al.* [3] and the dithiocarbamate complex $Mo_2O_3I_2(dtc)_2(THF)_2$ (**I**) reported by us [4], see Fig. 1. Both of these types of compounds accept oxygen atoms from oxygen donor species such as pyridine-*N*-oxide to produce MoO_2^{2+} complexes. In addition, **I** catalyzes the oxidation of triphenylphosphine by pyridine-*N*-oxide by interconversion of $Mo_2O_3^{4+}$, MoO_2^{2+} and MoO^{2+} species as shown in Scheme 1. Both the Schiff base and dtc compounds have in common the fact that they have a labile solvent molecule bound *trans* to a terminal oxygen–molybdenum double bond. In the case of **I** X-ray crystallography shows that the MoO(THF) bond is quite long [5]. This suggests that the THF is only weakly bound to the metal and that it may in fact be dissociated in solution. It is important to know whether or not an empty coordination site is available where O-donors may initially bind prior to atom transfer when formulating mechanisms of oxygen atom transfer reactions in which $Mo_2O_3^{4+}$ complexes participate. We have recently completed an NMR study of **I** and several of its other Lewis base adducts in an attempt to determine the degree to which the solvent molecule is dissociated when these complexes are in solution. The results of this study are reported in this paper.

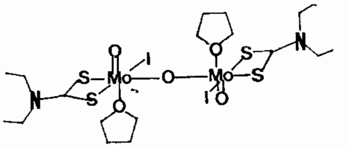

Fig. 1. Structure of $Mo_2O_3I_2(dtc)_2(THF)_2$.

Experimental

Materials and Methods

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Compound **I**, $Mo_2O_3I_2(dtc)_2(THF)_2$, was synthesized by a previously reported method [5]. $Mo_2(dtc)_6$ was synthesized from $MoO(dtc)_2$ using the method of Mitchell and Scarle [6]. Tetrahydrofuran and 1,4-dioxane were refluxed over Na/benzophenone under argon. Tetrahydrothiophene was degassed with Ar prior to use. Furan was distilled under an argon atmosphere. Acetonitrile was dried by repeatedly refluxing over phosphorous pentoxide. Thiophene was refluxed over $LiAlH_4$ and collected by distillation under argon. Pyridine was refluxed with solid NaOH and then distilled under argon. Methylene chloride was refluxed over CaH and was distilled just prior to use.

NMR spectra were run in $CDCl_3$ using either a Varian EM-360L or GE QE-300 spectrophotometer. Electronic spectra were obtained in CH_2Cl_2 using a

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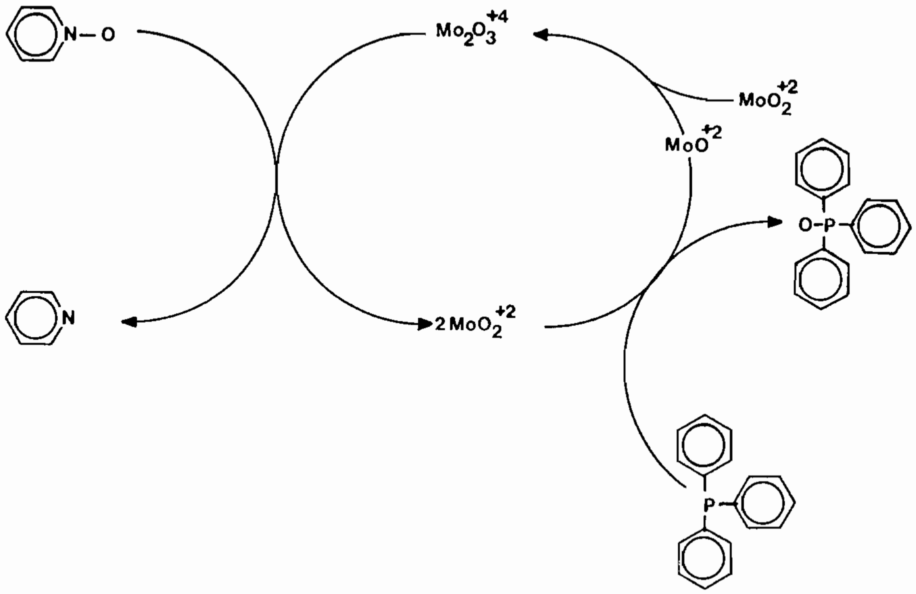

Scheme 1.

Shimadzu UV-2100 spectrophotometer. All NMR and electronic absorption samples were prepared under inert conditions using either Schlenk techniques or a Vacuum Atmospheres glove box. Infrared spectra were recorded using KBr pellets and a Matson Alpha Centauri spectrophotometer. Elemental analyses were performed at Atlantic Microlabs, Atlanta, GA.

Syntheses and Reactions

Synthesis of $Mo_2O_3I_2(dtc)_2(THT)_2$

$Mo_2O_3I_2(dtc)_2(THF)_2$ (**I**), 0.1 g, was dissolved in 15 ml of THT. This solution was stirred overnight. After a few days of refrigeration a black microcrystalline precipitate formed. This precipitate was isolated by filtration. Yield 82%. ^1H NMR ($CDCl_3$): 1.5(m), 1.9(m), 2.8(m), 4.0(m). IR: (Mo=O) 968 cm^{-1}. λ_{max} 486, 614 nm.

Synthesis of $Mo_2O_3I_2(dtc)_2(diox)_2$

A total of 0.1 g of **I** was dissolved in 20 ml of dioxane. This solution was allowed to stir overnight. The black precipitate which formed was isolated by filtration. Yield 87%. ^1H NMR ($CDCl_3$): 1.5(m), 3.7(s), 4.0(m). IR: (Mo=O) 980 cm^{-1}. λ_{max} 489, 614 nm. *Anal.* Calc. for $C_{18}H_{36}N_2S_4O_7Mo_2I_2$: C, 22.36; H, 3.73; I, 26.29. Found: C, 21.59; H, 3.66; I, 25.19%.

Reactions of I with acetonitrile, furan and thiophene

In each case 0.1 g of **I** was stirred overnight in 10 ml of the appropriate solvent. A black precipitate formed after refrigeration which was collected by filtration. The same product was obtained from all three reactions. The ^1H NMR spectra displayed methyl and methylene resonances at 1.5 and 4.0 ppm due to dtc, but neither solvent nor THF resonances were observed. IR: (Mo=O) 978 cm^{-1}. λ_{max} 488, 616 nm.

Reaction of I with pyridine

A total of 0.1 g of **I** was dissolved in 15 ml of pyridine. After stirring overnight a red solution resulted. Addition of an equal volume of hexane and refrigeration resulted in the formation of dark red needle-like crystals. λ_{max} 354, 445, 523 nm.

Results and Discussion

The reactions were carried out by dissolving **I** in the pure solvent followed by precipitation of the product. These reactions fell into three categories. Type I reactions were with solvents which have coordinating strengths approximately the same as THF. These reactions produced complexes in which the THF molecules had been replaced by the solvent in question. Type II reactions were with solvents which have lower coordinating ability than THF. These reactions gave complexes in which the THF had been removed but no solvent molecule replaced it. There was one type III reaction studied using pyridine which is more strongly coordinating than THF. This reaction resulted in a more complicated product in which no Mo=O bonds were detected by infrared spectroscopy.

Type I Reactions

In these reactions **I** was dissolved in either dioxane or tetrahydrothiophene, THT. In each case a complex, $Mo_2O_3I_2(dtc)_2(solv)_2$, was isolated. It is believed that the initially formed product contains both solvent bound to Mo and solvent molecules of crystallization. Both the THT and dioxane complexes initially form with solv/dtc ratios greater than 1. However, extended periods under vacuum at room temperature eventually result in solv/dtc ratios which reach unity. On the other hand, continued vacuum fails to lower this ratio any further. NMR spectra of the THT complex in $CDCl_3$ contain resonances due to THT. These, however, occur at 1.9 and 2.8 ppm, positions which correspond to those of free THT. The fact that the solv/dtc ratio cannot be reduced lower than 1 indicates that the THT is in fact bound to the molybdenum in the solid state. On the other hand, the NMR evidence seems to indicate that the THT is dissociated in chloroform solution. This notion is supported by a report from Templeton and McCarley which includes the NMR spectrum of $Ta_2Cl_6(THT)_3$ [7]. The structure of this complex includes two terminal and one bridging THT. The resonances associated with both types of coordinated THT molecules are shifted from those of free THT.

A similar result has been obtained for the THF complex. Extended vacuum lowers the THF/dtc ratio to 1. It has been shown by X-ray crystallography that there are in fact two THF molecules per $Mo_2O_3^{4+}$ unit [5]. The NMR verifies that THF is present in the complex but the resonances correspond to those of free THF with multiplets centered at 1.9 and 3.5 ppm. It would be expected that if the THF were still bound to the molybdenum in solution that its resonances would be shifted. In fact, we have previously reported the NMR spectrum of $Mo_2(Pdtc)_4(THF)_2$ in which both free and metal bound THF is present [8]. The resonances of the bound THF occur at 3.12 and 1.24 ppm while those of the free THF occur at 3.72 and 1.86 ppm.

Perhaps the most convincing example is that of the dioxane adduct of **I**. The NMR spectrum of this species indicates a dioxane/dtc ratio of 1 after extended vacuum, see Fig. 2. The resonance due to dioxane is a sharp singlet occurring at 3.7 ppm. This resonance frequency is the same as that of free dioxane. However, the fact that a singlet results is a clear indication that the dioxane is dissociated from the complex in chloroform. It would be anticipated that coordination through one of the oxygen atoms would result in inequivalence of the protons and thus a complex multiplet would be observed. It seems possible that the dioxane may be acting as a bridging ligand between two molybdenum atoms $Mo_2O_3I_2(dtc)_2(diox)_2$. Even if this were the case a singlet would not be expected, however. The singlet in free dioxane is a result of a boat–chair equilibrium similar to that known for cyclohexane. This equilibrium would probably not be fast on the NMR time scale if the dioxane were bound to two metal complexes.

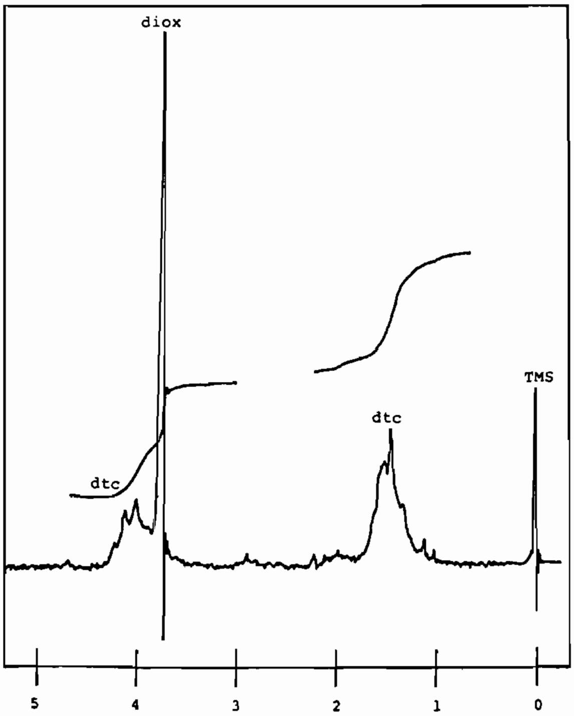

Fig. 2. ^1H NMR spectrum of $Mo_2O_3I_2(dtc)_2(diox)_2$ in CDCl.

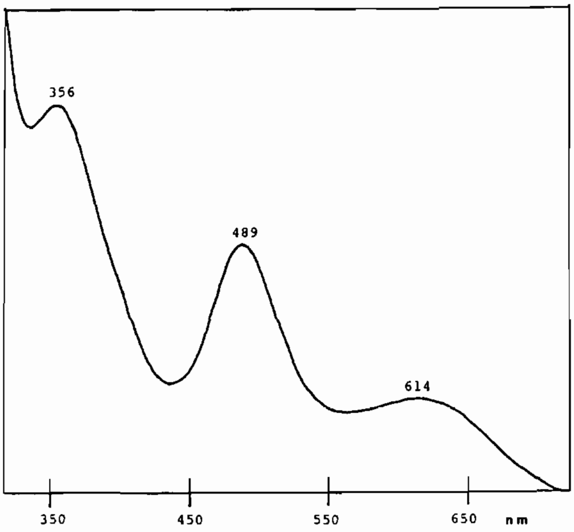

Fig. 3. Typical electronic absorption spectrum, in CH_2Cl_2 solution, obtained from products of type I and type II reactions.

Comparison of the electronic spectra of the THF, THT and dioxane complexes supports the idea that the solvent molecules are dissociated from $Mo_2O_3I_2(dtc)_2(solv)$ in methylene chloride solution, see Fig. 3. All three complexes display the same electronic spectrum. Thus the absorbing species is the same in all three cases. This would be the case if the solvent molecules were dissociated.

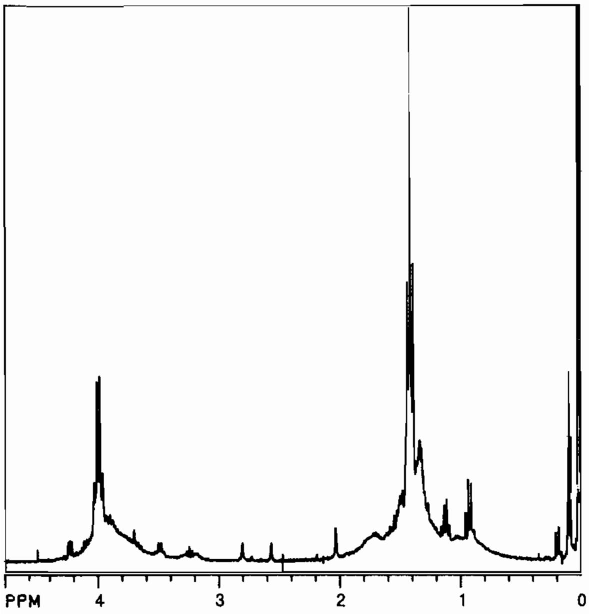

Fig. 4. ^1H NMR spectrum typical of products of type II reactions.

Type II Reactions

These reactions also indicate that THF is largely dissociated from **I** when it is in solution. Dissolution of **I** in acetonitrile, furan or thiophene results, after refrigeration, in isolation of the same dark solid in each case. NMR spectra show that neither THF nor solvent molecules are present in this complex, see Fig. 4. However, dtc resonances are still present centered at 1.4 and 4.0 ppm. It seems reasonable to propose that this material is oligomeric in the solid state with some sort of Mo–O–Mo interactions. This sort of structure has been proposed for non-solvated MoO_2L species where L is a tridentate Schiff base [9]. However, it appears that, unlike the MoO_2^{2+} compounds, in solution coordinatively unsaturated $Mo_2O_3I_2(dtc)_2$ is the predominant species in our case. This material exhibits an electronic spectrum in CH_2Cl_2 which is identical with those of the products of the type I reactions. This indicates that the $Mo_2O_3^{4+}$ core is still present. Indeed, the absorbing species in solutions of the product of type II reactions is undoubtedly the same as that in solutions of the THF, THT and diox adducts.

Type III Reactions

Dissolution of **I** in pyridine results in a bright red solution from which a highly air-sensitive red solid can be obtained. Infrared spectra of this compound do not possess the characteristic Mo=O stretching band in the 900–1000 cm^{-1} region. The electronic spectrum of this complex differs from the spectra of the products of the type I and type II reactions, see Fig. 5(A). In this case a pattern results with bands at 354, 445 and 523 nm in order of decreasing intensity. This spectrum is nearly identical to that produced from solutions of the red Mo(III) dithiocarbamate complex $Mo_2(dtc)_6$ which results from the reaction of $MoO(dtc)_2$ with triphenylphosphine in chloroform, see Fig. 5(B). $Mo_2(dtc)_6$ results from a disproportionation reaction in which $Mo_2O_4(dtc)_2$ is also formed.

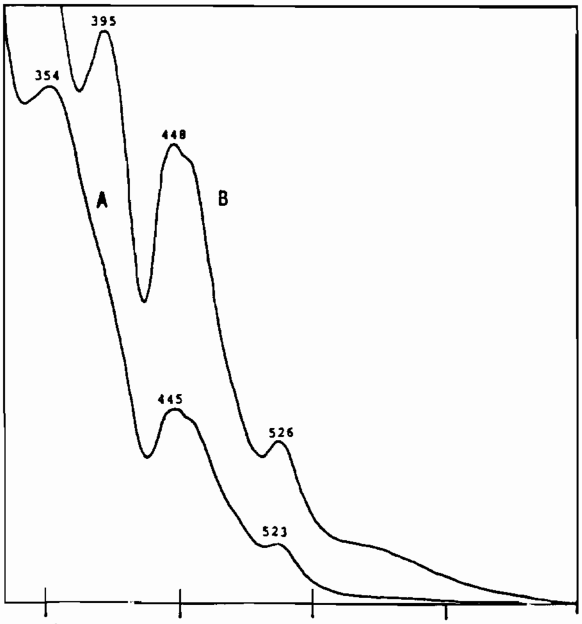

Fig. 5. (A) Electronic absorption spectrum of the product of **I** with pyridine. (B) Electronic absorption spectrum of $Mo_2(dtc)_6$.

The product of the reaction of **I** with pyridine has not yet been fully characterized, but it seems clear that a species other than that formed in the type I and type II reactions results. Available data suggest that this compound has no Mo=O bonds and may very well be a Mo(III) species similar to $Mo_2(dtc)_6$. This seems reasonable since the oxo-transfer reactions of **I** are similar to those of MoO^{2+} type complexes.

Conclusions

With weakly coordinating solvents such as those in the type II reactions the coordinatively unsaturated $Mo_2O_3I_2(dtc)_2$ results. With moderately coordinating solvents $Mo_2O_3I_2(dtc)_2(solv)_2$ species are isolated as solids, but in solution $Mo_2O_3I_2(dtc)_2$ also results. In each case a species is present which possess open coordination sites which are available for oxygen atom donors such as aromatic N-oxides or sulfoxides to bind prior to oxygen transfer. When more strongly coordinating solvents such as pyridine are used a more complicated product is obtained which probably has no oxo-transfer chemistry.

Acknowledgement

The support of the Research Corporation is gratefully acknowledged.

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