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DIOXYGEN BINDING AND ACTIVATION BY A NEW MOLYBDENUM (II) POLYNUCLEAR COMPLEX

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Summary

A new dimolybdenum(II) compound has been synthesized and characterized by physical methods including g.l.c., i.r., n.m.r., mass and X-ray spectrometry. The compound contains a very short (2.079 Å) Mo-Mo quadruple bond.

This complex is able to coordinate dioxygen directly and to use this activated molecule to oxidize ligand groups.

Introduction

Many transition metal complexes have received considerable attention because of their ability to form dioxygen adducts [1 - 3]; the metal atoms which have been reported are principally those of Group VIII, as well as Cr, Mn and Cu.

In addition to their interest as biochemical models, the most significant property of dioxygen complexes is their potential ability to catalyze the oxidation of organic substrates. Indeed, several important heterogeneous oxidation processes in which molybdenum-based catalysts are preferentially used [4, 5] are actually exploited in industry.

Until now the dioxygen complexes of molybdenum have been prepared by the reaction of suitable derivatives with hydrogen peroxide [6], and they have proved to be very active for the selective epoxidation of olefins [5, 7, 8].

We have recently been able to synthesize such an oxygenated molybdenum complex by direct coordination of dioxygen at room temperature, and to use this activated bonded oxygen to oxidize coordinated groups. In this paper, we report the structure of the molybdenum complex, and the first results of our studies on the oxygen activation process.

Results and discussion

(i) Preparation and characterization of the molybdenum complex

A double alkoxide of Mo and Al has been synthesized by thermal condensation between Al(III) isopropoxide and Mo(II) acetate, in a 1:1 molar ratio decalin. Upon sublimation at 160 °C (10^{-3} Torr), a pure orange crystalline compound has been obtained: it is very soluble in hydrocarbon solvents, and is both moisture and dioxygen sensitive.

Elemental analysis indicates the formula $\text{MoAlC}_{14}\text{H}_{31}\text{O}_6$, and a cryoscopic molecular weight determination in benzene suggests a dinuclear structure (theor.: 836; found: 790 ± 40). Moreover, after hydrolysis by acids, g.l.c. analysis demonstrates the presence of four isopropoxy groups (experimental result = 4.1) per Mo atom in the molecule.

The experimental oxidation state of Mo is +2, as shown by redox titrations using KMnO_4 . The compound is diamagnetic ($\chi_g = -0.28 \times 10^{-6}$ cgsu) between 77 and 300 K.

In agreement with the elemental analysis and cryoscopic determinations, the mass spectrum shows a strong parent ion, $[\text{Mo}_2\text{Al}_2\text{C}_{28}\text{H}_{62}\text{O}_{12}]^+$, together with many other dimolybdenum fragments corresponding to the loss of $\text{C}_3\text{H}_7\text{O}$ and CH_3COO groups, and of $(\text{C}_3\text{H}_7)_2\text{O}$ molecules, as expected from the chemistry of this type of derivative. All these dimolybdenum ions produce a very characteristic isotopic distribution pattern [9, 10].

The dinuclear, diamagnetic nature of this compound, together with the abundance of Mo_2 -containing ions in the mass spectrum, provide good evidence for the existence of a strong Mo-Mo bonding.

The infrared spectrum of the complex exhibits absorption bands characteristic of both terminal and bridging isopropoxy groups [11]. Moreover, the small gap (110 cm^{-1}) between symmetric (1550 cm^{-1}) and anti-symmetric (1440 cm^{-1}) COO stretching frequencies points to a bidentate coordination of the acetate groups [12].

The ^1H -n.m.r. spectrum consists of a complex multiplet centered at $\delta = 4.51$, a singlet ($\delta = 2.72$), and a set of two doublets ($\delta = 1.43$ and 0.97) (δ in ppm vs. TMS). The singlet was assigned to the methyl group of the acetate ligands, and the other peaks to the isopropyl groups; integration of peak areas show that the molecule contains 1 acetate for 4 isopropoxy groups. In addition, the presence of two doublets (CH_3) of equal intensities indicates that two distinguishable isopropoxy groups are present in the molecule in a 1:1 ratio. The complex multiplet, assigned to CH protons, is composed of two septuplets, as proved by double resonance. Moreover, the spectrum of the chlorobenzene solution remained unchanged in the range 240 - 370 K (except for a very slight broadening of the peaks).

Furthermore, the ^{13}C -n.m.r. spectrum is in complete agreement with the results obtained by ^1H -n.m.r. Distinct carbon resonances for bridging and terminal groups are observed at room temperature, i.e., 25.9 and 28.3 ppm vs. TMS for CH_3 , and 63.4 and 69.0 ppm vs. TMS for CH.

All these results have been confirmed by X-ray diffraction studies. Figure 1 represents the spatial configuration of the molecule: it is centrosymmetric, and the central Mo_2O_8 skeleton corresponds to an approximate D_{4h} symmetry. One of the most interesting results is the very short distance between the two Mo atoms, i.e., 2.079 Å. It is among the shortest known [13], and to our present knowledge only preceded by the 2.065 Å distance in $\text{Mo}_2[2.6\text{-C}_6\text{H}_3(\text{OCH}_3)_2]_4$ [14]. This result can be correlated with a very strong Mo-Mo quadruple bond.

(ii) Reaction with dioxygen

When a solution of $\text{Mo}_2\text{Al}_2\text{C}_{28}\text{H}_{62}\text{O}_{12}$ prepared under argon is exposed to dioxygen, a rapid color change from orange to dark brown is observed. Dioxygen absorption in *o*-dichlorobenzene at 300 K reaches an O_2 :Mo molar ratio of 1 within three hours. We have also observed that it is not a reversible process, even under vacuum at 400 K.

The reaction has been followed by gas-volumetric measurements of the dioxygen absorbed. This manometric method is not very accurate, and the kinetic parameters could not be evaluated with great precision. Nevertheless, we have determined, by the initial rate method, partial kinetic orders of 1.1 ± 0.1 and 0.9 ± 0.1 for Mo and dioxygen, respectively. A current order

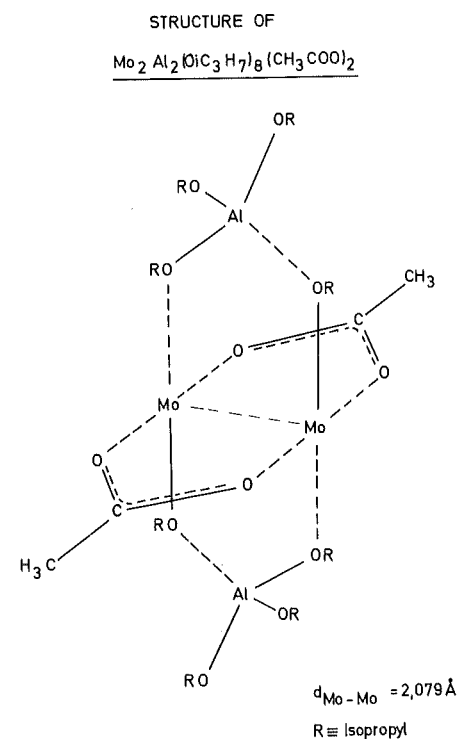


Fig. 1.

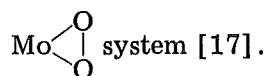
of 1 in Mo, and a corresponding rate constant k_{obv} equal to $(8 \pm 1)10^{-4} \text{ s}^{-1}$ at 298 K, have also been deduced.

The activation parameters, estimated from the Arrhenius equation are $\Delta H^* = 12\,000 \text{ cal mol}^{-1}$, and $\Delta S^* = -30 \text{ eu}$. The reaction between Vaska's complexes and dioxygen is characterized by similar activation enthalpies and entropies [15].

After a longer period of time (several hours) the solution of the complex turns light brown corresponding to a transformation of the dioxygen adduct with the formation of acetone (as detected by g.l.c.). For example, the evolution of 0.5 mole of acetone per Mo atom is observed after a period of 3.5 h at 300 K without any increase of the coordinated dioxygen amount. It is also interesting to note that small amounts of acetone can already be detected in the mixture during the first stages of the dioxygen absorption; this precludes the isolation of a perfectly pure oxygenated complex.

After evaporation of the solvent and volatile oxidation products, the oxygenated compound has been shown to have the formula $\text{MoAlC}_{11}\text{H}_{25}\text{O}_7$. It is not volatile so that the mass spectrum could not be recorded.

On the other hand, the i.r. spectrum indicates that the mode of binding of the carboxylate groups correspond to a bidentate structure [12] ($\nu_{\text{COO}} \text{ sym} - \nu_{\text{COO}} \text{ antisym} = 150 \text{ cm}^{-1}$). It also shows the presence of several absorption bands in the region $890 - 1\,000 \text{ cm}^{-1}$ which are characteristic of $\text{Mo}=\text{O}$ vibration modes: this is in agreement with similar bands reported in the literature [16, 17]. In addition, we have also observed characteristic absorption bands at 840 and 540 cm^{-1} which are usually assigned to $\text{O}-\text{O}$ and $\text{Mo}-\text{O}$ vibrations in a

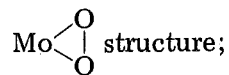


From redox titrations using the KMnO_4 standard procedure, Mo(IV) was found to be the dominant resulting species. The presence of peroxo groups was evidenced by iodometric titration.

It seems also that one molecule of the generated acetone remains weakly bonded to the complex, as suggested by cryoscopic measurements (molecular weight found = 470 ± 30 , calculated = 450) on a benzenic solution of the oxygenated compound, as well as by n.m.r. spectrometry.

Consistent with all these experimental results, the reaction between the dimolybdenum complex and dioxygen can be summarized as follows:

(a) as a first step, dioxygen is coordinated on the molybdenum atom giving a cyclic peroxo



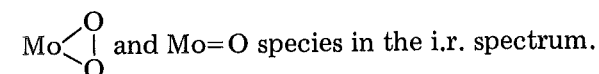
(b) in a second and maybe simultaneous step, corresponding to a complex rearrangement, there is a dissociation of the dinuclear compound resulting from the weakening of the $\text{Mo}-\text{Mo}$ bond upon coordination of dioxygen. This result completes, moreover, the previously reported obser-

vations of Cotton [18] on the sensitivity of the $\text{Mo}-\text{Mo}$ quadruple bond to axial coordination of additional ligands;

(c) in the third and final step, a slow, irreversible oxidation of the isopropoxy groups into acetone takes place (see Scheme I).

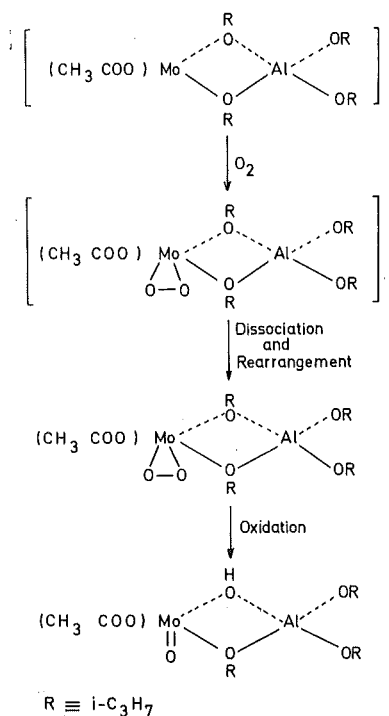
It is worthwhile to note that the formation of acetone is probably not due to the abstraction of an hydride ion from the α -CH group of an isopropoxy ligand (β -elimination process) [19, 20]. Despite the fact that the formation of acetone in our reaction appears only in the presence of dioxygen, we have never observed the formation of hydride complexes.

On the other hand, the oxidation mechanism proposed for the isopropoxy group above, is also supported by the presence of both



Conclusions

The foregoing observations represent, to our knowledge, a new type of dioxygen binding by a dimolybdenum complex with further use of this activated dioxygen in a ligand oxidation reaction. At present, only one related example has been reported by Arzoumanian [21], but this reaction was probably initiated by the Co(II) species present in the molecule.



Scheme I

The reported oxidation of the OR groups represents also an interesting model of oxygen transfer in a coordination sphere rearrangement; mechanistic studies using isotopically labeled molecules are in progress to clarify its mechanism.

Finally, this new procedure could lead eventually to an additional method for oxidizing alcohols [22 - 26] if a suitable regeneration of the resulting OH ligand back into an OR one could be found. The more interesting case would be the conversion of n.OR groups into aldehydes, an indication of which has already been obtained with iron complex alkoxides [27].

Acknowledgments

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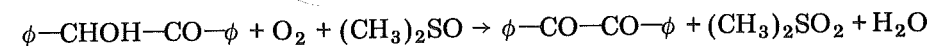
AUTOXIDATION OF BENZOIN COUPLED TO THE OXYGENATION OF THE SOLVENT BY AN OXOCUPRIC COMPLEX IN DIMETHYL-SULFOXIDE

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Summary

The catalytic activity of the autoxidation product of $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ in dimethylsulfoxide (DMSO) on the oxidation of benzoïn to benzil was studied. The stoichiometry for this reaction is:



according to that of mixed function oxidases. The cuprous salt, as well as its autoxidation product in DMSO, was used as a catalyst. The kinetics of the oxidation were measured by monitoring the oxygen uptake manometrically or by means of an oxygen electrode. A mechanism explaining these kinetic results is proposed and parallels to biological systems are discussed.

Introduction

The interest in copper-catalyzed oxidations of organic substrates arises both from their potential as a tool in synthesis [1 - 3] and from their model character for certain redox enzymes [4]. The cuprous chloride/pyridine system has been particularly well studied and more than a dozen papers have appeared during the last few years [1 - 3, 5 - 7].

During our studies of the autoxidation of simple cuprous complexes we found that the autoxidation product of cuprous perchlorate or tetrafluorate in DMSO is a versatile redox catalyst [8]. Three reactions were studied in more detail by means of product analysis and kinetics. Good yields of about 80% were obtained for the oxidative coupling of 2,6-dimethylphenol to poly(2,6-dimethyl-1,4-phenylene ether), for the oxidation of 3,5-di-*t*-butylcatechol to 3,5-di-*t*-butyl-*o*-benzoquinone, and for the oxidation of benzoïn to benzil [8]*. Here we intend to discuss specifically the last of these reactions and its relation to the autoxidation of monovalent copper in DMSO.

* $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ in pyridine is stable towards O_2 . However, autoxidation starts as soon as equimolar amounts of chloride are added. Autoxidized solutions thus prepared are redox catalysts and a solid catalyst was isolated [9, 10].