JOURNAL OF CATALYSIS 152, 237–242 (1995)

Catalytic Air Oxidation of Thiols Mediated at a Mo(VI)O$_2$ Complex Center Intercalated in a Zn(II)–Al(III) Layered Double Hydroxide Host

Avelino Corma,*,[1] Vicente Fornés,* Fernando Rey,* Antonio Cervilla,† Elisa Llopis,†
and Antonio Ribera†

Instituto de Tecnología Química, U.P.V.-C.S.I.C., Universidad Politécnica de Valencia, Avenida de los Naranjos, s/n, 46071 Valencia, Spain; and †Departament de Química Inorgánica, Universitat de Valencia, Dr. Moliner 50, 46100 Burjassot (Valencia) Spain

Received May 9, 1994; revised October 24, 1994

While bis(2-mercapto-2,2-diphenyl-ethanoate) dioxomolybdate (VI), $\{MoO_2[OOCC(S)(C_6H_5)_2]_2\}^{2-}$ (I), ethanolic solutions stoichiometrically react with aromatic and aliphatic thiols to give the corresponding disulfides, the intercalation of I within a Zn(II)–Al(III) layered double hydroxide (LDH) allows their catalytic oxidation by dioxygen. A reaction scheme is proposed in which a $Mo^{IV}O$ species activates O_2, regenerating the parent $Mo^{VI}O_2$ complex (I), which then acts as a true catalyst. Kinetic data for the thiol oxidation reaction have been determined. The results obtained here demonstrate that the intercalation of I into a Zn(II)–Al(III) LDH host inhibits the formation of catalytically inactive $Mo^{V}O$ species that are always formed under homogeneous conditions.

INTRODUCTION

Studies on the chemical mechanism of molybdenum hydroxylases have give considerable impetus to the elaboration of the chemistry of oxomolybdenum complexes in the oxidation state (VI), (V) and (IV) (1, 2). Their catalytic properties critically depend on the formation of catalytically inactive Mo(V) species through the reaction $Mo^{VI}O_2L + Mo^{IV}OL \rightleftharpoons Mo^{V}O_3L_2$. From current evidence, this comproportionation reaction always occurs unless it is sterically prevented (3, 4).

In a previous work (5, 6), we have shown the capability of the bis(2-mercapto-2,2-diphenyl-ethanoate) dioxomolybdate (VI) complex, $\{MoO_2[OOCC(S)(C_6H_5)_2]_2\}^{2-}$ (**I**), to oxidize thiols (PhSH). However, the comproportionation reaction between **I** and its reduced $Mo^{IV}O$ complex leads to the formation of the monomeric molybdenum (V) complex $\{Mo^{V}O[OOCC(S)(C_6H_5)_2]_2\}^{-}$, according to

$$\begin{aligned} &\{Mo^{VI}O_2[O_2CC(S)(C_6H_5)_2]_2\}^{2-} \\ &\quad + \{Mo^{IV}O[O_2CC(S)(C_6H_5)_2]_2\}^{2-} + 2H^+ \\ &\quad \rightarrow 2\,\{Mo^{V}O[O_2CC(S)(C_6H_5)_2]_2\}^{-} + H_2O. \end{aligned} \qquad [1]$$

Such a particular feature implies an important limitation to the catalytic properties of **I**. In fact, contrary to all $Mo^{IV}O$ complexes tested so far, the $\{Mo^{V}O[OOCC(S)(C_6H_5)_2]_2\}^{-}$ complex shows no reducing capacity on common oxidants such as dialkyl S-oxides, amine N-oxides, and dioxygen.

It becomes apparent to us that suppression of reaction [1] could be achieved by fixing complex **I** on a solid surface. Since both $Mo^{IV}O_2$ and $Mo^{IV}O$ complexes have an anionic character, we thought that one possibility consists in the intercalation of **I** into a cationic layered double hydroxide host such as a hydrotalcite material.

Layered double hydroxides (LDH) consist of positively charged brucite-like layers separated by charge-balancing hydrated gallery anions (7). A broad range of compositions of the type $[M^{2+}_{3-x}M^{3+}_{x}(OH)_6][A^{n-}]_{x/n}\cdot yH_2O$ ($x = 0.51$–1) are possible, wherein M^{2+} and M^{3+} are the cations in octahedral positions of the hydroxide layers and A^{n-} is an exchangeable anion positioned between these layers (8). Recent advances in the pillaring of LDH by polyoxometallate anions have demonstrated that these microporous materials exhibit large gallery heights suitable for catalytic oxidation of organic compounds (9). Their preparation, properties, and applications have been reviewed recently (10).

Most of the polyoxometallates intercalated in LDH have been prepared by ion exchange methods. Specifically, well-ordered Zn(II)–Al(III)-LDHs incorporating the polyoxometallate anions $V_{10}O_{28}^{6-}$ or α-1, 2, 3-$[SiV_3W_9O_{40}]^{7-}$ have been obtained by ion exchange reactions with simple LDH precursors of the type Cl^-–LDH and NO_3^-–LDH (11, 12). However, since exchange reactions can be slow, particularly with large anions, other procedures have also been developed. Thus, the intercalation of the cobalt (II) phthalocyaninetetrasulfonate complex $(CoPcTs)^{4-}$ in a Mg(II)–Al(III) LDH was carried out by interaction of solid $Mg_{0.63}Al_{0.25}$¤$_{0.12}O$ (¤, vacancy), pre-

---

[1] To whom correspondence should be addressed.

0021-9517/95 $6.00

pared by the thermal decomposition of $[Mg_5Al_2(OH)_{14}][CO_3] \cdot x\ H_2O$ at 773 K, with an aqueous solution of the $[CoPcTs]^{4-}$ ion (13). In catalyzing the air oxidation of thiols at alkaline pH (9.25), this intercalated Co(II) complex was twice as active as the homogenous complex under equivalent reaction conditions and concentrations.

In the present work, we will show that reaction [1], responsible for the catalyst deactivation, can be suppressed by introducing the molybdenum complex **I** into the interlamellar space of a Zn(II)–Al(III) hydrotalcite-type structure. Under these conditions, the intercalated complex **I** can also oxidize thiols to disulfide but the reduced complex now has the ability to react with O_2 returning to its oxidized $Mo^{VI}O_2$ parent form.

EXPERIMENTAL

Characterization of Hydrotalcite-like Compounds

The NO_3^--LDH precursor and the intercalated catalyst (**I**-LDH) were characterized by powder X-ray diffraction (XRD), thermogravimetry (TGA) and differential thermal analysis (DTA), diffuse reflectance (DR), and infrared spectroscopy (IR). XRD spectra were carried out using Cu*Kα* radiation with a Philips PW 1830 at a scanning speed of 2.4° min^{-1}. FTIR and UVDR spectra were recorded in Nicolet 710 and Shimadzu UV-2101 PC spectrometers, respectively. Thermal analyses were undertaken with a thermobalance STA 409 NETZSCH, using α-Al_2O_3 as reference material.

The reaction course was monitored by gas chromatography (GC), using a 15-m phenilmethilsilicone semicapillary column with a FID detector. Products were identified by gas chromatography mass spectroscopy (GCMS).

The possibility of diffusion control was checked out by changing the stirring speed. The same rate for the PhSH/PhS–SPh conversion was obtained at 700 and 1500 rpm, indicating that no control by external diffusion exists under the above reaction conditions.

RESULTS AND DISCUSSION

Synthesis and Characterization

As a precursor material, (NO_3^--LDH) was prepared by the following procedure. A solution containing 97.03 g of $Zn(NO_3)_2 \cdot 4H_2O$) (0.36 *M*) and 45.93 g of $Al(NO_3)_3 \cdot 9H_2O$ (0.12 *M*) in 180 ml of water was mixed dropwise with another solution prepared by dissolving 31.02 g of NaOH (0.76 *M*) and 54.95 g of $NaNO_3$ (0.64 *M*) in 235 ml of water to obtain a gel of the following composition:

$$2.25\ Zn(NO_3)_2 : 0.75\ Al(NO_3)_3 : 4.75\ NaOH : 4\ NaNO_3.$$

The resulting slurry had a pH of 8. It was transferred to a stainless-steel autoclave, in which crystallization took place under autogenous pressure at 353 K for 18 h. The solid was then filtered and washed until NO_3^- ions were not detected in the washing water, and afterward it was dried at 340 K overnight to obtain 41.5 g of NO_3^--LDH.

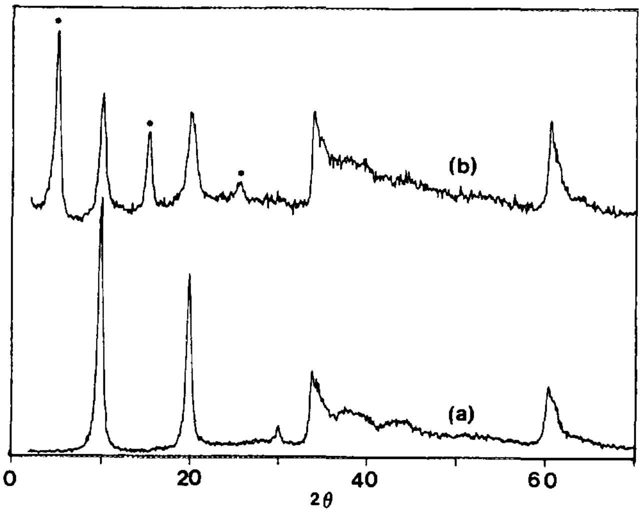

FIG. 1. X-ray powder patterns of (a) NO_3-LDH and (b) **I**-LDH. Peaks marked with an asterisk are assigned to the basal space between sheets when the molybdenum complex is intercalated.

The X-ray power diffraction pattern for NO_3^--LDH, Fig. 1a, shows two sharp peaks indexed as (003) and (006) at 8.9 and 4.45 Å, respectively, by assuming the rombohedral symmetry previously assigned by Miyata (14) to a similar material. No other phase was observed in this XRD pattern, indicating that only nitrate ions are intercalated in the Zn–Al hydroxide layers. According to these results and from the chemical analysis obtained for the NO_3^--LDH precursor, given in Table 1, the following mineralogical formula can be written: $Zn_{2.20}Al_{0.79}(OH)_6(NO_3^-)_{0.79}\ H_2O$.

Partial substitution of intercalated nitrate ions by the complex **I** was achieved by addition of 24 g of the NO_3^--LDH precursor to an orange solution of 20.8 g of the sodium salt of complex **I** (29.2 mmol) in 2 liters of a glycol–methanol–water (1 : 1 : 1) mixture, followed by stirring at room temperature for 48 h. The resulting yellowish solid was then washed with methanol and dried in

TABLE 1

Chemical Analysis for NO_3-LDH and I-LDH

	Al (%)	Zn (%)	Mo complex (%)	Weight loss (%)
NO_3-LDH	7.43	50.16	—	37.97
I-LDH	4.84	32.08	20.57	39.22

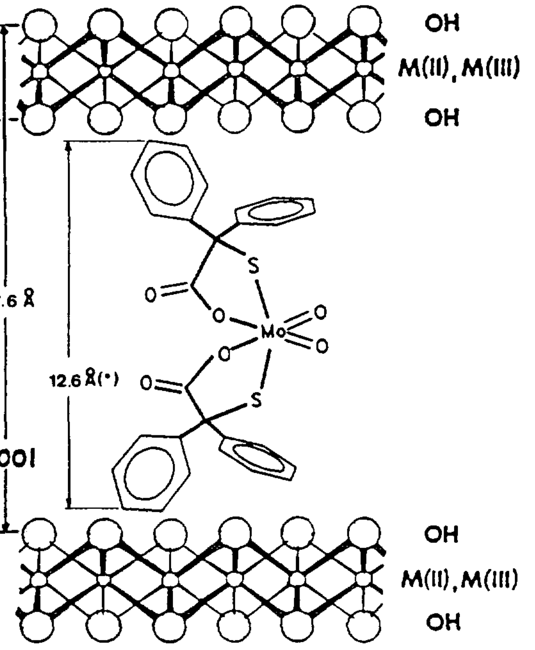

FIG. 2. Schematic illustration of the orientation of **I** intercalated in LDH. The value marked with an asterisk was calculated from the molecular structure of **I**, which was previously established by X-ray crystallography.

the oven at 340 K for 18 h, giving 26 g of **I**-LDH described under Experimental. The chemical analysis of the resultant catalyst (Table 1) indicates that ~32% of the NO_3^- was substituted by **I**. Moreover, it can also be observed a negligible change in the Al/(Al + Zn) ratio when the Mo complex was exchanged by nitrate ions, indicating that no leaching of either Al or Zn has occurred during this anion exchange procedure.

The XRD of the exchanged material shows a decrease in the intensity of the two peaks assigned to the NO_3^--LDH phase, accompanied by the appearance of three new peaks at 17.6, 8.8, and 5.8 Å (see Fig. 1b). From these new (001) harmonics, characteristics of a pillared LDH phase, a basal spacing of 17.6 Å was calculated. Since the Van der Waals thickness of the brucite sheets is ca. 4.7 Å (15), the calculated basal spacing was indicative of a gallery height of ca. 12.9 Å. Such a value, together with other previous parameters found in a single crystal of the ammonium salt of **I**, seems to indicate that the dianionic complex **I** possesses its C_2 axis parallel to the metal hydroxide layers as shown in Fig. 2. In this orientation, both terminal oxo groups bonded to Mo(VI) can interact with potential substrates in gallery centers, away from the Zn–Al oxygen layers.

While a methanolic solution of **I** exhibits only one band at 374 nm (6), the UV–V spectrum of **I**-LDH displays two bands at 356 and 275 nm with an absorbance ratio of $A_{356}/A_{275} = 2.5$. Both absorptions must be considered in character as ligand to metal charge transfer bands, since the Mo(VI) center does not have any electron in 4*d* orbitals.

Compared to NO_3^--LDH, thermogravimetric analysis of a **I**-LDH sample showed two additional exothermic peaks at ca. 660 and 806 K (Fig. 3) that must be assumed to be caused by the decomposition of complex **I** in MoO_3, CO_2, and H_2O. The weight loss corresponding to this decomposition is ca. 39.22%, which agrees with the chemical composition resulting from elemental analysis for this **I**-LDH sample, which is expressible by the formula $Zn(II)_{2.20}\ Al(III)_{0.80}\ (OH)_6\ (NO_3^-)_{0.54}\ (\mathbf{I})_{0.13}\ H_2O$ (see Table 1).

Finally, the IR spectrum for NO_3^--LDH showed a sharp and strong band at 1382 cm^{-1} that arises from the ν_3 stretching mode of NO_3^-, while the water molecules exhibit a broad bending band ν_2 near 1630 cm^{-1} (16). The IR spectrum of the yellowish **I**-LDH product contained bands characteristic of the parent NO_3^--LDH and the intercalated complex **I**. Thus, the appearance of new bands at 900 cm^{-1} (Mo=O) and 1600 cm^{-1} (coordinated carboxylate groups from the ligands) constitutes a clear indication of the presence of **I** into the Zn(II)–Al(III) LDH host.

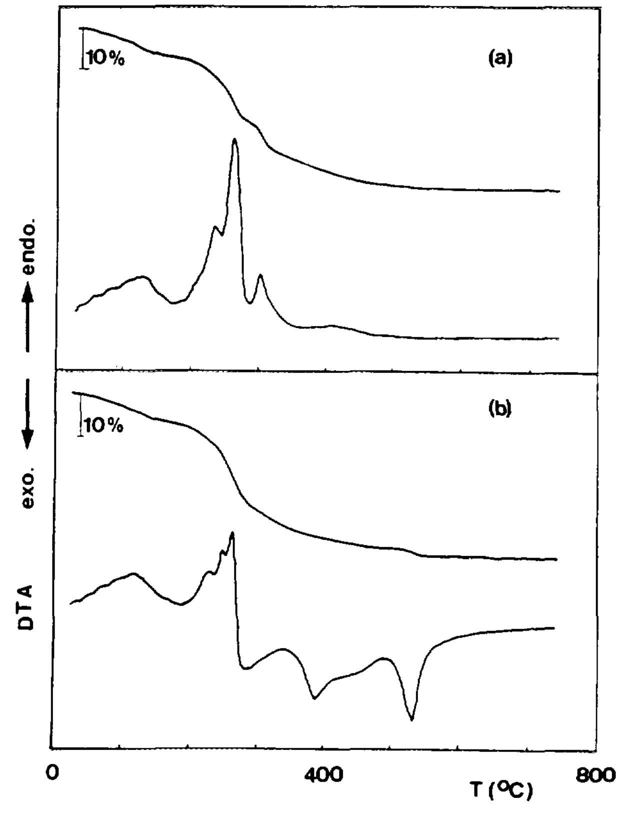

FIG. 3. (a) DTA and TGA curves for NO_3-LDH. (b) DTA and TGA curves for **I**-LDH.

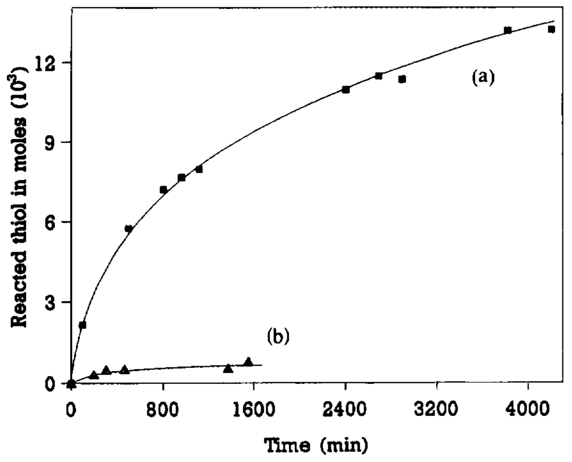

FIG. 4. Thiophenol (× 10^3 mol) oxidized by (a) O_2 (P_{O_2} = 1 atm) and (b) air (P_{air} = 1 atm) vs time at T = 353 K in EtOH (20 ml). The initial concentration of C_6H_5SH is 3.1 g (28 mmol) in LDH-**I** (250 mg, 20.57% in **I**) plus protonic amberlite IR-120(H) (250 mg).

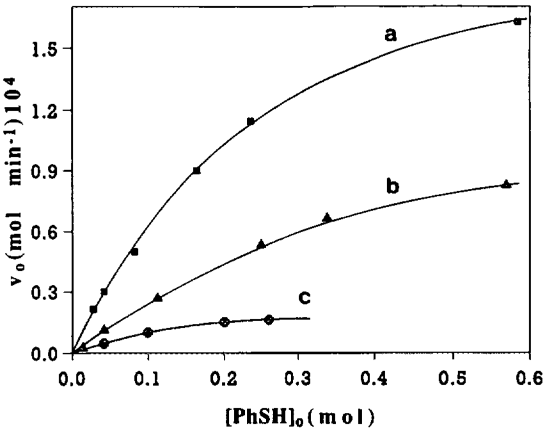

FIG. 6. Variation of the initial rate for the oxidation of C_6H_5SH by O_2 vs initial amount of C_6H_5SH. Partial pressure of O_2 1 atm, in EtOH (20 ml) LDH-I (250 mg, 20.57% in **I**) plus protonic amberlite IR-120(H) (250 mg) at (a) 353 K, (b) 333 K, and (c) 313 K.

Catalytic Properties

Reactions were carried out in a 50-ml flask equipped with a condenser. In a typical experiment, 0.25 g of **I**-LDH and 0.25 g of amberlite IR 120 (H) were added to 20 ml of ethanol containing different amounts of thiophenol (from 0.01 to 0.58 mol) under air or pure O_2 at atmospheric pressure. Amberlite was introduced to act as a proton source that facilitates the outcoming of the oxo group initially bonded to the Mo (VI) atom of complex **I**.

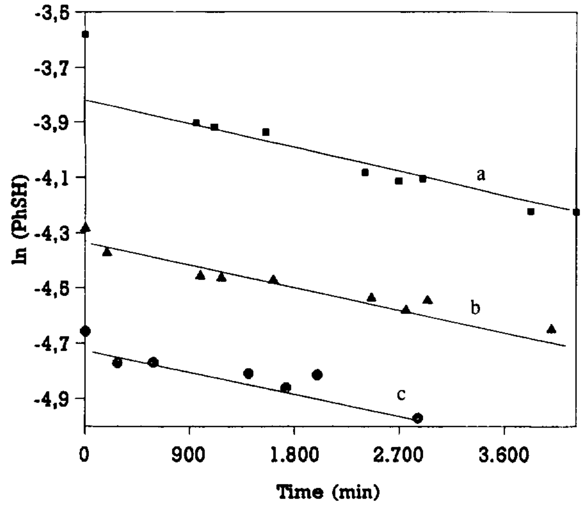

FIG. 5. Pseudo-first order kinetic plots for the reaction between C_6H_5SH and O_2 at 353 K in EtOH (20 ml). The initial concentration of C_6H_5SH is (a) 3.15 g (28.0 mmol), (b) 1.57 g (14, 0 mmol), and (c) 1.08 g (9, 6 mmol) in LDH-**I** (250 mg, 20.57% in **I**) plus protonic amberlite IR-120(H)(250 mg).

The initial pH of the solution was ca. 4.7 and remained constant throughout the reaction.

While no oxidation of PhSH was detected in the presence of NO_3^--LDH and protonic amberlite, the complete oxidation of all PhSH to disulfide rapidly proceeded if **I**-LDH was present in the solution. Figure 4 shows the variation in the consumed PhSH vs time, when pure O_2 or air was used as oxidant. Clearly, the catalytic rate depends on the oxygen pressure upon the solution.

While the detailed mechanism of this catalytic reaction is not yet certain, the following observations severely limit the possibilities. First, the PhSH oxidation rate depends on both dioxygen and thiophenol concentrations and also on the amount of **I**-LDH catalyst. Second, a first order law with respect to PhSH concentration was obeyed only at a determined P_{O_2} and catalyst concentration, when PhSH is present in a low concentration. Taking these features together and having demonstrated previously that **I** is capable of oxidizing thiols to the corresponding disulfides (6), we propose a mechanism for this catalytic reaction in terms of Eqs. [2]–[4], in which a transient $\{Mo^{IV}O[O_2CC(S)(C_6H_5)_2]_2\}^{2-}$ complex is the species reactive toward dioxygen.

$$\begin{aligned}&\{Mo^{VI}O_2[O_2CC(S)(C_6H_5)_2]_2\}^{2-}\text{-LDH}\\ &+ PhSH \xrightarrow{K_1} \{Mo^{IV}O[O_2CC(S)(C_6H_5)_2]_2\}^{2-}\text{-LDH} \quad [2]\\ &\qquad + PhS^+ + OH^-\end{aligned}$$

$$\left(PhS^+ + OH^- \xrightarrow[PhSH]{\text{very fast}} PhSSPh + H_2O\right) \quad [3]$$

$$\begin{aligned}&\{Mo^{IV}O[O_2CC(S)(C_6H_5)_2]_2\}^{2-}\text{-LDH}\\ &+ 1/2\, O_2 \xrightarrow{K_2} \{[Mo^{VI}O_2[O_2CC(S)(C_6H_5)_2]_2\}^{2-}\text{-LDH}. \quad [4]\end{aligned}$$

TABLE 2

Temperature Dependence of the Reaction Rates of I-LDH plus PhSH

T(K)	K_a (min^{-1})	K_a/[Mo] (min^{-1}mol^{-1})
353	8.2396×10^{-4}	9.8
333	2.3209×10^{-4}	2.8
313	1.3682×10^{-4}	1.6

It is completely justified on the basis of previous results (1, 20, 21) to assume that oxygen abstraction from complex **I**, Eq. [2], is slower than the reoxidation process [4], in which O_2 is used as oxidant. Thus, the following catalytic rate expression can be proposed:

$$-\frac{d[\mathrm{PhSH}]}{dt} = K_1\,[\mathrm{PhSH}]\,[\mathbf{I}]. \tag*{[5]}$$

On the basis of the above mechanism and by applying a steady state approximation for the concentration of the reduced $\{\mathrm{Mo^{IV}O[O_2CC(S)(C_6H_5)_2]_2}\}^{2-}$ complex, Eq. [5] becomes

$$-\frac{d[\mathrm{PhSH}]}{dt} = \frac{K_1\,K_2\,[\mathrm{Mo}]\,[\mathrm{O_2}]^{1/2}\,[\mathrm{PhSH}]}{K_1\,[\mathrm{PhSH}] + K_2\,[\mathrm{O_2}]^{1/2}}, \tag*{[6]}$$

in which [Mo] is a constant value that represents the total concentration of complexed Mo intercalated into LDH, **I** plus $\{\mathrm{Mo^{IV}O[O_2CC(S)(C_6H_5)_2]_2}\}^{2-}$.

At relatively low or moderate concentrations of PhSH, it can be assumed that $K_1\,[\mathrm{PhSH}] \ll K_2\,[\mathrm{O_2}]^{1/2}$ and, consequently, Eq. [6] yields:

$$-\frac{d[\mathrm{PhSH}]}{dt} = K_1\,[\mathrm{Mo}]\,[\mathrm{PhSH}] = K_a[\mathrm{PhSH}]. \tag*{[7]}$$

This last equation shows a pseudo-first order dependence in thiol concentration that is consistent with the results presented in Fig. 5. In addition, when the initial PhSH oxidation rate is plotted vs the initial PhSH amount, Fig. 6, the plot deviates from linearity only at sufficiently high thiol amount (>0.2 mol).

Alternatively, the rate data of Fig. 6 may be displayed in the form of a double-reciprocal plot. A very good linear correlation (correlation coefficient > 0.99) displays the linear behavior required by Eq. [6]. The value of K_1[Mo], equal to K_a, was determined from the slope of this $1/v_0$ vs $1/(\mathrm{PhSH})_0$ representation. Table 2 shows the value of K_a at three different temperatures, together with the activity of **I**-LDH per Mo atom.

The activation energy of reaction [2] was calculated from an Eyring plot of ln k vs $1/T$, utilizing the K_a rate constants in Table 2. The obtained 9.8 kcal mol^{-1} value is very close to that of 9.6 kcal mol^{-1} reported for other representative systems such as $\mathrm{MoO_2(L{-}NS_2)}$ plus $\mathrm{Et_3P}$ (22).

CONCLUSIONS

To our knowledge, this study constitutes the first report of a molybdenum-based catalyst for the oxidation of thiols by molecular oxygen. The bulk of our results concerning the catalytic activity of **I**-LDH are consistent with **I** being the active oxidant and a transient $\mathrm{Mo^{IV}O}$ species the active reductant. Formation of a mononuclear $\mathrm{Mo^{V}O}$ species such as that previously observed under homogeneous conditions (reaction [1]) can be ruled out since such a species has been shown to decompose immediately in the presence of dioxygen. Our results demonstrate the potentialities of intercalation into LDH as a new strategy to prevent the formation of monomeric and dimeric $\mathrm{Mo^{V}}$ species. Such a strategy is probably of general applicability to anionic complexes as an alternative to the use of sterically hindered bulky ligands (3).

An important advantage of the intercalation strategy consists in the fact that water can be used as a solvent. To our knowledge, all $\mathrm{Mo^{VI}O_2}$ catalytic systems previously studied require the use of aprotic solvents, and even then the water generated during the oxidation of thiols or benzoin precipitates and/or decomposes the molybdenum catalyst.

ACKNOWLEDGMENTS

A. R. thanks Generalitat Valenciana for a postgraduate scholarship. A. C. acknowledges DGICYT for financial support (Grants 89-0417 and MAT 94-0359-CO2-01). We also thank the European Communities, Directorate General XII (MASIMO program) for financial assistance.

REFERENCES

1. Holm, R. H., *Chem. Rev.* **87,** 1401 (1987).
2. Holm, R. H., *Coord. Chem. Rev.* **100,** 133 (1990).
3. Berg, J. M., and Holm, R. H., *J. Am. Chem. Soc.* **107,** 917 (1985).
4. Berg, J. M., and Holm, R. H., *J. Am. Chem. Soc.* **107,** 925 (1985).
5. Palanca, P., Picher, T., Sanz, V., Gomez-Romero, P., Llopis, E., Doménech, A., and Cervilla, A., *J. Chem. Soc. Chem. Commun.* 531 (1990).
6. Sanz, V., Picher, T., Palanca, P., Llopis, E., Ramirez, J. A., Beltran, D., and Cervilla A., *Inorg. Chem.* **30,** 3115 (1991).
7. Almann, R., *Chimia* **24,** 99 (1970).
8. Miyata, S., *Clays Clay Miner.* **28,** 50 (1980).
9. Tatsumi, T., Yamamoto, K., Tajima, H., and Tominaga, H., *Chem. Lett.*, 815 (1992).
10. Cavani, F., Trifiro, F., and Vaccari, A., *Catal. Today.* **11,** 173 (1991).
11. Kwon, T., Tsigdinos, G. A., and Pinnavaia, T. J., *J. Am. Chem. Soc.* **110,** 3653 (1988).

12. Dimotakis, E. D., and Pinnavaia, T. J., *Inorg. Chem.* **29,** 2393 (1990).
13. Pérez-Bernal, M. E., Ruano-Casero, R., and Pinnavaia, T. J., *Catal. Lett.* **11,** 55 (1991).
14. Miyata, S., *Clays Clay Miner.* **23,** 369 (1975).
15. Elleman, D. D., and Williams, D., *J. Chem. Phys.* **26,** 742 (1956).
16. Nakamoto, K., *in* "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed., p. 88. Wiley, New York, 1970.
17. Cardonna, J. P., Reddy, P. R., and Holm, R. H., *J. Am. Chem. Soc.* **110,** 2139 (1988).
18. Newton, W. E., Corbin, J. L., Braward, D. C., Searles, J. E., and McDonald, J. W., *Inorg. Chem.* **13,** 1100 (1974).
19. Barral, R., Bocard, C., Roch, S., and Sajus, L., *Tetrahedron Lett.*, 1963 (1972).
20. Ueyama, N., Yano, M., Miyashita, H., Nakamura, A., Kamachi, M., and Nozakamura, S., *J. Chem. Soc. Dalton Trans.*, 1447 (1984).
21. Ueyama, N., Yoshinaga, N., and Nakamura, A., *J. Chem. Soc. Dalton Trans*, 387 (1990).
22. Schultz, E. B., Holm, R. H., *Inorg. Chem.* **32,** 4244 (1993).