RATES AND MECHANISM OF THE STOICHIOMETRIC OXIDATIONS OF ORGANIC SULPHIDES TO SULPHOXIDES WITH THE PEROXOMOLYBDENUM COMPLEX MoO(O₂)₂HMPT

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Summary

Stoichiometric oxidations of various organic sulphides were performed in 1,2-dichloroethane at -15 °C with the oxodiperoxocomplex MoO(O₂)₂-HMPT in the absence and in the presence of Hg(OCOCF₃)₂. The oxidation catalyzed by this salt displays an enhancement in rate of three orders of magnitude with respect to the uncatalyzed process. The relevance of these findings in the mechanistic analysis of oxygen transfer process from peroxometal complexes to organic substrates is discussed.

Introduction

Recently, we reported a novel catalytic effect by the mercuric ion in the oxidation of alkynes by molybdenum and tungsten peroxocomplexes [1]. In particular, we observed that in the presence of mercuric acetate or trifluoroacetate, $MoO(O_2)_2HMPT$ smoothly oxidizes alkynes to dicarbonyl compounds in dichloroethane, whereas in the absence of added mercuric salts no reaction takes place. Owing to the general relevance of such an oxidation, and also from a synthetic standpoint, we deemed it worthwhile to investigate in further detail the role played by the mercuric catalyst in oxygen transfer processes from peroxometal complexes.

To this aim, we have selected a model reaction, the oxidation of organic sulphides, which has been extensively studied in several systems [2]. An advantage connected with the choice of such a model reaction is the possibility of comparing the behavior of the uncatalyzed oxidation with that of the catalyzed one.

The kinetic and spectroscopic results presented and discussed here confirm that mercuric salts behave as catalysts also in sulphide oxidations.

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Furthermore, it appears that the catalytic effect, rather than arising from a ground state interaction between the substrate and the catalyst, should be attributed to an electrophilic catalysis by the mercuric salt in the transition state.

Results and discussion

The oxidation of the model sulphide Ph–S–CH₃ to the corresponding sulphoxide by MoO_5HMPT in dichloroethane (DCE) at -15 °C proceeds both in the absence and in the presence of Hg(CF₃CO₂)₂, providing quantitative yields of the oxidized product. Therefore, the stoichiometry of the uncatalyzed and catalyzed processes is as follows:

$$MoO_5HMPT + 2Ph-S-CH_3 \longrightarrow MoO_3 + HMPT + 2Ph-S(O)CH_3$$
 (1)

The kinetics were studied under pseudo-first-order conditions by using an excess of the substrate over the oxidant.

Pseudo-first-order plots of the uncatalyzed processes were linear for at least three half-lives. In the presence of the mercuric salt, deviations from linearity after one half-life were observed, likely due to the occurrence of side reactions such as the decomposition of the peroxide.

Control experiments have shown that added mercury does also catalyze the decomposition of the peroxometal complex. However, under our experimental conditions, the effect of such a process on the overall rate of sulphoxide formation, particularly in the first 50% reaction, may be neglected.

A first-order dependence of rates on both substrate and oxidant was observed. Second-order rate constants k_2 of the oxidation of a series of arylalkyl sulphides are collected in Table 1.

As to the catalyzed reaction, the pertinent kinetic data are reported in Table 2. A third-order rate law is observed, first order in the substrate, oxidant and catalyst. A plot of k_{obs} vs. [Hg] shows in all cases an intercept whose value, divided by substrate concentration, agrees reasonably well with the rate constants k_2 of the uncatalyzed reactions measured in separate experiments (Table 1). Therefore, the rate law of the catalyzed oxidation of sulphides is:

(2)

$$R = k_2[Sub][Ox] + k_3[Sub][Ox][Hg]$$

where k_3 is the third-order rate constant.

A rate acceleration caused by addition of mercury is clearly observed. Under otherwise identical experimental conditions, the k_{obs} of the oxidation of Ph—S—Me is 4.2×10^{-4} s⁻¹ in the absence of added catalyst, whereas a value of 77×10^{-4} s⁻¹ is observed when 5.7×10^{-3} M of Hg(CF₃CO₂)₂ is added.

Reactivity ratios k_3/k_2 in Table 2 indicate that the catalytic presence of the mercuric salt causes an increase in the oxidation rate of three orders of magnitude for a 1 M concentration of the catalyst.

TABLE 1

x–	М	$\frac{10^3 \times k_{obs}}{(s^{-1})}^{b}$	$10^2 \times k_2^{e}$ (M ⁻¹ s ⁻¹)
CH₃—	0.022 0.043 0.086	3.09 6.55 12.5	14.6
H—	0.016 0.032 0.041	0.42 1.23 1.53	4.51
Cl—	0.011 0.021 0.041	0.173 0.444 0.922	2.48
NO ₂ —	0.032 0.059 0.119	0.122 0.196 0.410	0.336

Rate constants for the stoichiometric oxidation of X-Ph-S-CH₃ to sulphoxides with MoO(O₂)₂HMPT in DCE at -15 °C, under nitrogen^a

^aThe reactions were carried out in a total volume of 50 ml.

^bObtained from the slopes of $\ln[O]_{act}$ vs. time; $[O]_{act} = 2[MoO_5HMPT]$.

^cObtained from the slopes of plots of k_{obs} vs. [sulphide]₀.

The rate constants of Table 1 and 2, referring to the oxidation of four aryl-substituted arylalkyl sulphides, increase with increasing nucleophilicity of the substrate, *i.e.* $NO_2 < Cl < H < CH_3$. This is taken as a clear evidence that the sulphide is the nucleophilic partner of the oxidation reaction. On this basis, it is unlikely that the catalytic effect of the mercuric salt results from a coordination process involving the substrate and the catalyst. Indeed, such a coordination would reduce the nucleophilicity of the sulphide and an inhibitory, rather than a catalytic effect, should be expected. On the other hand, the possibility of coordination between sulphides and mercuric species is documented in the literature [3]. By ¹H NMR spectroscopy, we have obtained direct evidence of an interaction between arylalkyl sulphides and Hg(CF₃COO)₂ in CDCl₃ at -15 °C. In particular, addition of Hg(CF₃COO)₂ (0.1 mmol) to a solution of Ph—S—Me (0.1 mmol) causes a downfield shift of the resonances of the methyl group of Ph—S—Me from $\delta = 2.45$ ppm to $\delta = 3.02$ ppm and an increase in the multiplicity of the aromatic protons.

By varying the sulphide/Hg ratio from 1 to 5, a continuous change in the chemical shift is observed from 3.02 ppm to 2.61 ppm. This is an indication that we are dealing with a fast equilibrium process, and also suggests that the association constant of the sulphide to the mercuric salt is not particularly large.

Therefore, from these data, we may conclude that coordination of the sulphide to mercury takes place, although this cannot rationalize the catalytic effect observed.

x —	М	$10 \times Hg(OCOCF_3)_2$ (M)	$\frac{10^3 \times k_{obs}}{(s^{-1})}^{b}$	${^{k_{3}c}}_{(M^{-2} s^{-1})}$	${k_{3}/k_{2}}^{d}$ (M ⁻¹)
CH3-	0.010	0.010	3.5 7 3	251	
	0.019 0.010 0.010	0.010 0.024 0.016	7.0 4.8		1719
н—	0.020 0.033	0.014 0.014	2.0 2.8	65	1441
	0.052 0.020 0.021	0.014 0.007 0.057	5.4 1.2 7.7		
C1	0.019 0.032 0.050	0.015 0.015 0.015 0.015	1.9 2.8 5.4	58	2339
	0.019 0.019	0.027 0.058	3.6 6.8		
NO ₂ —	0.021 0.033 0.050	0.014 0.015 0.015	0.62 1.1 1.6	16	4762
	0.021 0.021	0.025 0.040	0.97 1.5		

Rate constants for the stoichiometric oxidation of $X-Ph-S-CH_3$ to sulphoxides with $MoO(O_2)_2HMPT$ in the presence of $Hg(OCOCF_3)_2$ in DCE at -15 °C, under nitrogen^a

^aThe reactions were carried out in a total volume of 50 ml.

^bObtained from the slopes of $\ln[O]_{act}$ vs. time, linear up to 50%.

^cObtained from the slopes of k_{obs} vs. [Hg(OCOCF₃)₂]; see eqn. (2).

 d_{k_2} values are those of Table 1.

On the other hand, some evidence of an interaction of the peroxometal complex with $Hg(CF_3COO)_2$ has been obtained. In particular, a hypochromic effect in the electronic spectrum of $MoO(O_2)_2HMPT$ at $\lambda = 310$ nm is observed. By contrast, ¹H NMR spectra of solutions of $MoO(O_2)_2HMPT$ in the presence of $Hg(CF_3COO)_2$ in CDCl₃ indicate that ligand exchange processes involving HMPT do not occur [4]. Therefore, the interaction is likely to involve either the oxo oxygen or the peroxide oxygens of the peroxo species.

On this basis, it might be concluded that Hg^{2+} exerts its catalytic effect in a fashion amenable to an electrophilic catalysis taking place in the transition state of the oxygen transfer process. Examples of rate acceleration caused by hydrogen bonding in the transition state of oxidations by peroxides are abundant.

Recently, we observed a similar effect on the epoxidation of geraniol and linalool with the very same oxidant [5].

TABLE 2

Experiments run in the presence of BF_3^* support this interpretation, since an acceleration of the oxidation rate of PhSCH₃ is observed also in this case.

The conclusion reached here, *i.e.* that substrate-mercuric ion complexation in the ground state may cause in fact an inhibitory effect, overcome by a catalytic effect in the transition state, may have relevance also in the definition of the mechanism of the Hg-catalyzed oxidation of alkynes by Mo and W peroxocomplexes.

Experimental

Materials

1,2-Dichloroethane was obtained by standard procedures from highly pure commercial samples. Phenylmethylsulphide, 4-chlorophenylmethyl sulphide and 4-methylphenylmethyl sulphide were prepared by methylation of the commercially available thiols as reported previously [2a]; 4-nitrophenylmethyl sulphide was obtained in the same way from the corresponding thiol, prepared according to reported procedures [6]; phenylmethyl sulphoxides were prepared from the corresponding sulphides by oxidation with H_2O_2/H^+ in ethanol and purified by recrystallization. $Hg(OCOCF_3)_2$ is a commercial chemical (Aldrich), which was used as received. Molybdenum(VI) oxodiperoxo complex $MoO(O_2)_2HMPT$ was prepared by the original procedure already reported [7].

Instrumentation and procedures

Gas chromatographic analyses of reaction mixtures were carried out on a Carlo Erba 2350 gas chromatograph equipped with a flame ionization detector and program capability. The identity of sulphoxides was confirmed by comparison with authentic samples. A 2 m column packed with OV-17 on 80/100 Supelcoport was used for product determinations.

Kinetic measurements

All kinetic runs were carried out under nitrogen atmosphere, following the disappearance of the oxidant by iodometric titrations. Blanket experiments indicate that the decomposition of the oxidant is a negligible process in the time scale of the oxidation reactions. Also, in the presence of the mercuric salt the oxidative process represents the main path which involves the oxidant, at least within the first 50% of reaction. Furthermore, at -15 °C in DCE a control experiment indicated that phenylmethyl sulphoxide does not react in the reaction conditions adopted for sulphide oxidations.

On the other hand, stoichiometric studies pointed out that sulphoxides are formed quantitatively according to eqn. (1). In fact 1 mmol of phenyl-

*[PhSCH₃] = 0.033 M, [BF₃·O(C₂H₅)₂] = 0.0014 M, $10^3 \times k_{obs}(s^{-1}) = 5.1$.

methyl sulphide reacts with 0.13 mmol of $MoO(O_2)_2HMPT$ in the presence of 0.08 mmol of mercuric trifluoroacetate at -15 °C to yield 0.22 mmol of sulphoxide.

The reactions followed pseudo-first-order kinetics up to 80% for the uncatalyzed process and 50% for the catalyzed process. Pseudo-first-order rate constants were evaluated using a linear least squares computer program.

Spectroscopic measurements

¹H NMR spectra were recorded using a Bruker WP-80 spectrometer with TMS as internal standard in CDCl₃. UV spectra were run on a Perkin Elmer 330 spectrophotometer in DCE, reagent for spectroscopy, at room temperature.

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