

CATIONIC COMPLEXES OF RHODIUM(I) AS CATALYSTS IN THE HOMOGENEOUS O₂-OXIDATION OF TERMINAL ALKENES TO METHYL KETONES

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(Received June 6th, 1984)

Summary

$[\text{Rh}(\text{LL})_2]^+$, $[\text{Rh}(\text{LL})(\text{diene})]^+$ and $[\text{Rh}(\text{LL})\text{S}_2]^+$ complexes are effective as catalysts for the oxidation by dioxygen of terminal olefins to methyl ketones. The complexes act as monooxygenases, the second oxygen atom being transferred to the alcohol solvent.

Introduction

The homogeneous oxidation of organic substrates by oxygen catalysed by transition metal complexes has been subject of a number of investigations in recent years, the aim having been both to increase the rate and selectivity and to determine the mechanism of these valuable reactions. Rhodium has proved a particularly suitable metal, and the most interesting results have been attained with the rhodium trichloride-copper(II) salts system, which is very effective catalyst for the selective O₂-oxidation of terminal olefins to the corresponding methyl ketones [1].

Since the primary function of the metal complex in oxygen transfer reactions is to coordinate molecular oxygen, our initial efforts involved $[\text{Rh}(\text{PSR})_2]^+$ complexes (PSR groups are bidentate hybrid ligands of the type $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{SR}$), which readily coordinate dioxygen to give 1:1 adducts with various stabilities [2]. It was hoped that, as had already been observed with other d^8 -metal complexes containing these PSR ligands [3–5], the sulfur could be removed from the coordination sphere of the metal and replaced by an olefin. Dioxygen and a π -coordinated olefin would both be present on one metal center, thus providing the opportunity for a monometallic oxygen transfer. In fact, the $[\text{Rh}(\text{PSR})_2]^+$ complexes were found to be effective in the catalytic oxidation of terminal olefins to methyl ketones [6], and the ligands were

stable towards oxidation over week-long experiments. This stability was particularly interesting, since usually with rhodium(I) complexes containing monodentate phosphines or arsines, which do promote the oxygenation of olefins, the ligands are oxidised, and so the oxygen transfer is not catalytic in rhodium unless free ligand is continually added to the systems [7–10].

In the present paper we discuss some mechanistic aspects of the oxidation reaction involving these and other cationic complexes of rhodium(I), i.e., the well-known $[\text{Rh}(\text{diphosphine})_2]^+$ and $[\text{Rh}(\text{diphosphine})(\text{diene})]^+$ derivatives, which have also been found to be active in the catalytic oxygen transfer reaction.

Experimental

The NMR spectra were recorded on a Bruker WP 60 spectrometer. GLC analyses were performed on a Perkin–Elmer Sigma 3B gas chromatograph. Mass spectra were recorded on a VG instrument.

Literature methods were used to prepare $[\text{Rh}(\text{COD})\text{Cl}]_2$ [11] and $[\text{Rh}(\text{diene})\text{acac}]$ [12]. The PSR ligands were prepared by reacting NaPPh_2 and the appropriate ω -chloro, or -bromo-alkyl sulphide ($\text{X}(\text{CH}_2)_n\text{SR}$) in liquid ammonia.

Alcohols were reagent grade and dried with 3Å molecular sieves. 1-Octene was distilled from LiAlH_4 . ^{18}O -oxygen (99%) and ^{18}O -water (50%) were purchased from Stohler Isotope Chemicals.

The dioxygen absorption was followed using a standard apparatus with a thermostatted gas-burette. A weighed amount of the catalyst was suspended on a side-arm in a teflon container and allowed to dissolve in the reaction mixture after equilibrium had been reached.

Preparation of $[\text{Rh}(\text{LL})_2]\text{BF}_4$ and $[\text{Rh}(\text{LL})(\text{diene})]\text{BF}_4$ (diene = COD, NBD)

To a solution of $[\text{Rh}(\text{diene})\text{acac}]$ in dichloromethane, a solution of the appropriate amount of the ligand LL was added at 0°C. Trityl tetrafluoroborate (1 equiv.) in dichloromethane was added and the yellow solution concentrated in vacuo. On the addition of diethyl ether, yellow crystals of the compounds separated and these were recrystallized from dichloromethane ether. The analytical data and characterization of the PSR derivatives are reported elsewhere [2,13].

Anal. Found: C, 49.13; H, 4.84; S, 11.06. $[\text{Rh}(\text{COD})(\text{PhSCH}_2\text{CH}_2\text{SPh})]\text{BF}_4$ calcd.: C, 48.56; H, 4.82; S, 11.76%.

Results and discussion

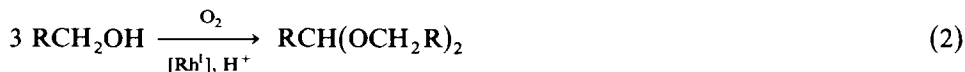
A number of complexes of type $[\text{Rh}(\text{LL})_2]\text{BF}_4$ and $[\text{Rh}(\text{LL})(\text{diene})]\text{BF}_4$ have been tested as catalysts for the oxidation of olefins, where the diene moiety is *cis,cis*-1,5-cyclooctadiene or norbornadiene, and LL are bidentate phosphines of the type $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1$, dpmm; $n = 2$, dppe; $n = 3$, dppp; $n = 4$, dpbb) and *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPH}_2$ (*cis*-dppet), or phosphorous-sulfur hybrid bidentate ligands of the type $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{SR}$ ($n = 1$, R = Ph (PSPH-C₁); $n = 2$, R = Ph (PSPH-C₂), R = Et (PSEt-C₂), R = Me (PSMe-C₂); $n = 3$, R = Ph (PSPH-C₃), R = Et (PSEt-C₃)), or the bidentate $\text{PhS}(\text{CH}_2)_2\text{SPh}$ (dpte).

All of the complexes examined were found to be more or less effective as catalysts for the O₂-oxidation of terminal olefins to methyl ketones under mild conditions

(25–70°C; 0.2–1 atm O₂) in acidic alcoholic media.



In the absence of the added acid the systems proved to be ineffective, apart from a few complexes containing the PSR ligands, which still promoted, though very slowly, the oxidation of the organic substrates. Also the solvent (a primary or secondary alcohol) is concomitantly and independently oxidized to the corresponding acetal or ketone.



The reaction profiles for the various rhodium(I) complexes are of the type shown, as an example, in Fig. 1: apart from the very early part of the reaction, where varying behaviour could be observed, straight lines were always obtained by plotting

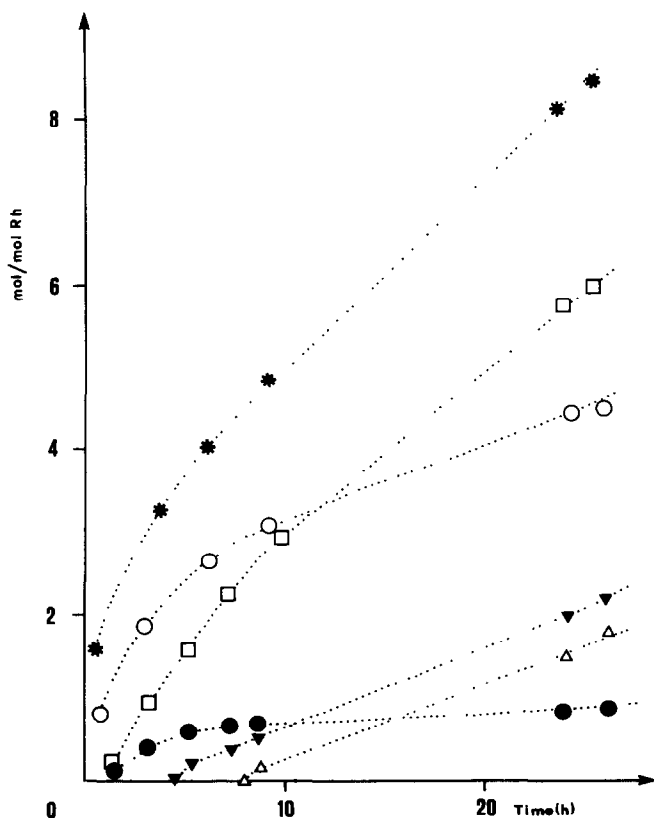


Fig. 1. Formation of 2-octanone from 1-octene (0.25 M) in CH₃OH (*T* 50°C, *P*(O₂) 1 atm, CH₃SO₃H (0.01 M)) in the presence of [Rh(LL)₂]BF₄ (0.01 M) (LL = dppm (O), dppe (□), dppp (Δ), dppb (▼), *cis*-dppet (●), PSPH-C₂ (*)).

the quantity of methyl ketone produced vs. time. The zero order in substrate (present in a 25-fold excess with respect to the catalyst) is satisfactorily maintained up to 10 turnovers. The catalytic activities of the rhodium(I) complexes, as given by the slope of the straight portion of the reaction profiles, are reported in Table 1. They are apparently affected by the nature of the chelate ring, rather than by the nature of the donor atoms, whereas no significant differences have been observed in general between the $[\text{Rh}(\text{LL})_2]^+$ complexes and the corresponding $[\text{Rh}(\text{LL})(\text{diene})]^+$ species. The complexes containing the rigid diphosphine *cis*-dppet are less active, by a factor of ten, than those containing the other bidentate ligands $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ and $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{SR}$. Also the only bithioether-derivative examined here, i.e. $[\text{Rh}(\text{dpte})(\text{COD})]\text{BF}_4$, has a relatively high activity [14]. The PSR- C_2 and the dppe complexes were found to be somewhat more reactive than those containing ligands with both shorter (PSR- C_1 and dppm) and longer (PSR- C_3 , dppp and dppb) carbon chains between the donor atoms, but the differences are far less dramatic. On the other hand, the rather low catalytic activity of the *cis*-dppet complexes could be related to the enhanced rigidity of the chelate ring, as has been observed for analogous complexes of rhodium(I) when acting as catalysts in the hydrogenation of olefins [15].

The generally comparable catalytic activity of the bis(chelate) $[\text{Rh}(\text{LL})_2]^+$ and mono(chelate) $[\text{Rh}(\text{LL})(\text{diene})]^+$ cations suggests that for both systems the same, or a closely related, catalytic species is operating, which may still contain the chelate ligand. Significantly, the $[\text{Rh}(\text{LL})\text{S}_2]^+$ derivatives generated in situ by the hydrogenation of the corresponding $[\text{Rh}(\text{LL})(\text{COD})]^+$ cations, also are effective in promoting the oxygen transfer reactions and, again, the *cis*-dppet derivative shows a distinctly lower activity (Fig. 2). This could indicate that a highly unsaturated species, namely $[\text{Rh}(\text{LL})\text{S}_2]^+$ itself, is actually responsible for the catalytic process in all of the cases examined. The intriguing induction times which have been observed in the oxidations promoted by the $[\text{Rh}(\text{diphosphine})_2]^+$ (Fig. 1) and also by the $[\text{Rh}(\text{LL})(\text{diene})]^+$ complexes, may indeed result for the fact that vacant sites are not easily available in the above species for the accomodation of the olefin and dioxygen and therefore some rearrangement is expected in order to produce the true catalyst.

TABLE 1

OXIDATION OF 1-OCTENE TO 2-OCTANONE IN THE PRESENCE OF RHODIUM(I) CATALYSTS^a (quoted in cycles h⁻¹)

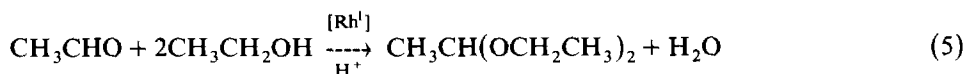
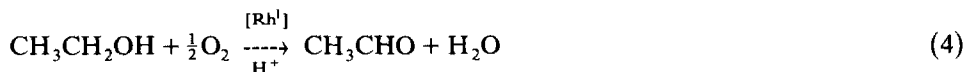
| LL | $[\text{Rh}(\text{LL})_2]\text{BF}_4$ | $[\text{Rh}(\text{LL})(\text{diene})]\text{BF}_4^b$ |
|--------------------|---|---|
| dppm | 0.09 | |
| dppe | 0.20, 0.12 ^c , 0.02 ^d | 0.04 |
| dppp | 0.09 | |
| dppb | 0.09 | |
| <i>cis</i> -dppet | 0.01 | 0.01 |
| PSPH- C_1 | 0.07 ^c | 0.09 ^{c,e} |
| PSPH- C_2 | 0.28, 0.16 ^c , 0.03 ^d | 0.22, 0.30 ^c , 0.04 ^d |
| PSPH- C_3 | 0.07 ^c | 0.07 ^{c,e} |
| dpte | | 0.12, 0.07 ^c , 0.01 ^d |

^a $[\text{Rh}^I]$ 0.01 M, [1-octene] 0.25 M, $[\text{CH}_3\text{SO}_3\text{H}]$ 0.01 M, 1 atm O₂, 50°C in methanol (unless otherwise stated). ^b diene = *cis,cis*-1,5-COD (unless otherwise stated). ^c In ethanol. ^d In 2-propanol. ^e diene = norbornadiene.

On the other hand, no induction times were found when the $[\text{Rh}(\text{PSR})_2]^+$ derivatives or, significantly, the cation $[\text{Rh}(\text{dppm})_2]^+$ were used. One can speculate that in these cases coordinatively unsaturated species can more easily be formed (the above ligands possibly acting as monodentate).

However, no direct evidences of such species, or of other unsaturated derivatives, could be obtained by ^{31}P NMR measurements on the reaction mixtures; these always shown that the starting complexes $[\text{Rh}(\text{LL})_2\text{O}_2]^+$ or $[\text{Rh}(\text{LL})(\text{diene})]^+$ are the dominant species [16].

Evidence for the involvement of dioxygen as the oxygen source in the methyl ketone formation has been obtained by carrying out the oxidation of 1-octene using a rhodium(I) complex in the presence of $^{18}\text{O}_2$. Since the solvent (ethanol) is also



oxidized to 1,1-diethoxyethane, with the formation of water, labelled water is produced in the presence of $^{18}\text{O}_2$ (99%) in reaction 4 (but not in reaction 5), with in theory, a 50% content of $^{18}\text{OH}_2$. The experimental enrichment was lower than this, due to the presence of a small amount of water in the solvent.

The formation of increasing amounts of water and particularly of ^{18}O -water during the reaction, makes interpretation of the isotopic experiments complicated, since a rapid ^{18}O -exchange occurs between water and the ketones [17]. Nevertheless, Fig. 3 clearly shows that the ^{18}O content of the oxidation product (2-octanone) and the added 2-hexanone are different at the beginning of the reaction, the former being much more enriched than the latter. After this, the oxygen-exchange process accounts for the overall distribution of ^{18}O between 2-octanone, 2-hexanone and water, all of which finally show an identical isotopic content. Related experiments, carried out in the presence of natural dioxygen and added ^{18}O -water indicate that there is no incorporation of ^{18}O in the 2-octanone produced apart the amount expected from the reversible hydration exchange, thus confirming that the oxidation reaction is a true O_2 -oxidation, and not a Wacker-type oxidation, of the olefin.

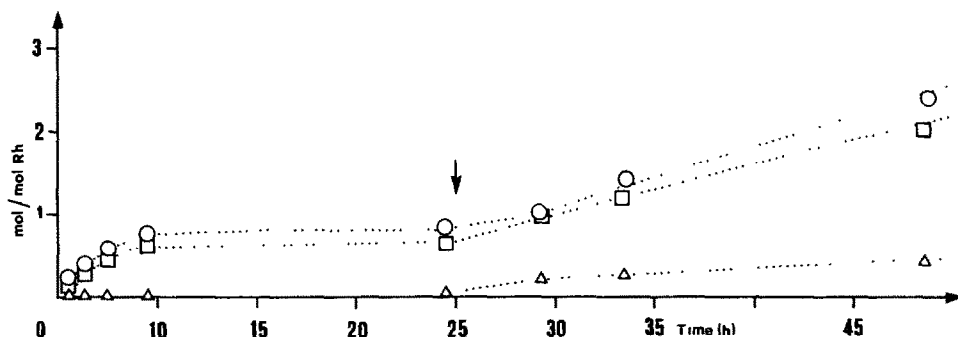
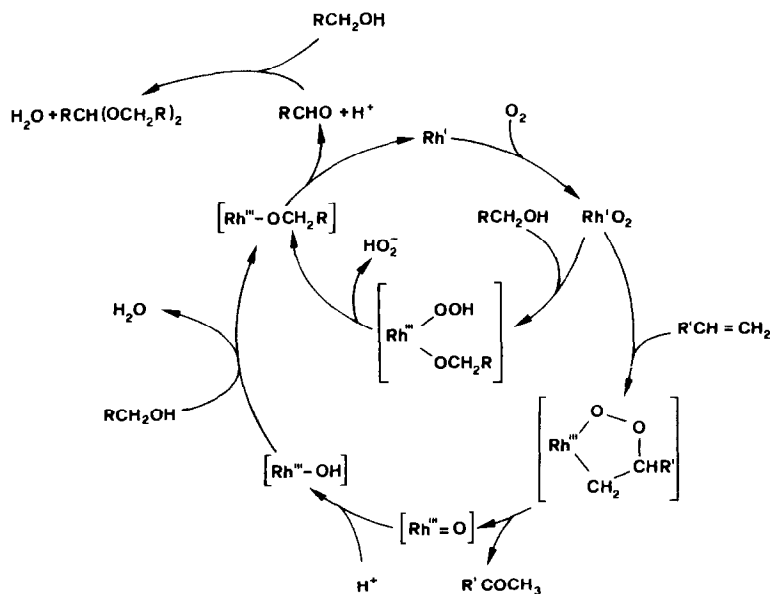


Fig. 2. Formation of 2-octanone from 1-octene (0.25 M) in CH_3OH (T 50°C, $P(\text{O}_2)$ 1 atm) in the presence of previously hydrogenated $[\text{Rh}(\text{LL})(\text{COD})]\text{BF}_4$ (0.01 M) (LL = *cis*-dppet (Δ), dppe (□), PSh-C₂ (○)). Arrow indicates addition of $\text{CH}_3\text{SO}_3\text{H}$ (0.01 M).

Measurements of the uptake of O_2 (see Fig. 4) do not permit an easy correlation to be made between the amount of absorbed dioxygen and the extent of the ketone formation, again because of the simultaneous oxidation of the solvent. A comparison can be made once the measured amount of absorbed oxygen is corrected for that portion involved in the oxidation of the solvent, assuming that 1 mol of O_2 is required to produce 2 mol of acetal. Moreover, since the 1:1 O_2 -adduct is the dominant organometallic species in solution (*vide infra*), this must be taken in account.

It turns out that the formation of 1 mol of 2-octanone roughly involves the consumption of 1 mol of O_2 (calculations give 0.8–0.9 mol of O_2 , rather than 0.5), thus ruling out a concerted transfer of both oxygen atoms to two molecules of olefin [18].

Since no other major products have been found during the oxidation, we suggest that the second oxygen atom is involved in the oxidation of a molecule of the alcohol, which gives the re-formation of the rhodium(I) catalyst and a closed



SCHEME 1

catalytic cycle (Scheme 1). Indeed, the oxidation of the olefin becomes catalytic only in the presence of oxidizable (primary and secondary) alcohols, whereas in non-oxidizable solvents, such as *t*-butyl alcohol, acetone or dichloromethane, stoichiometric, or nearly stoichiometric amounts, of the methyl ketones are formed (0.3–0.8 mol per mol of catalyst).

In Scheme 1, hydrogen peroxide is assumed to be the primary product of the oxygenation of the alcohols, as is usually observed for this class of metal-promoted reactions [19]. It is also well-established that metal complexes are effective catalysts for the disproportionation of H_2O_2 to O_2 and H_2O [20], and we found this with the reaction mixtures.

It is also possible that hydrogen peroxide, produced *in situ* by the oxidation of the alcoholic solvent, may be the actual oxidizing agent for the olefin, as recently

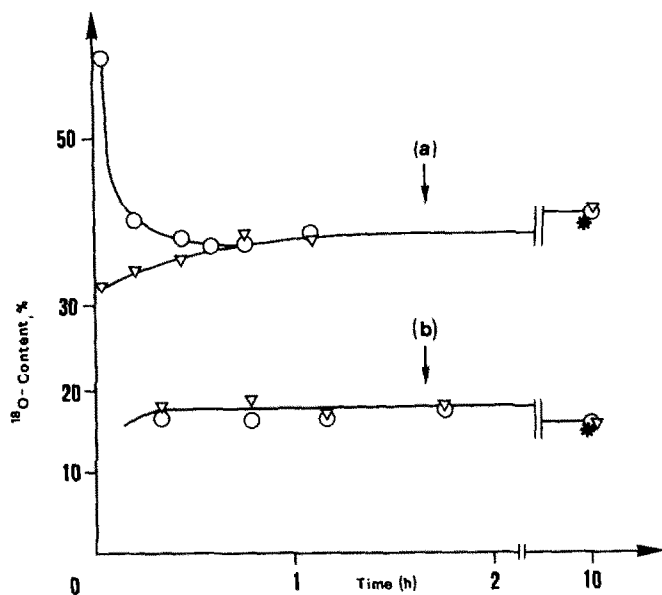


Fig. 3. ^{18}O Content for 2-octanone (\circ), 2-hexanone (∇) and water ($*$) during the oxidation of 1-octene (0.25 M) and ethanol (solvent) at 50°C in the presence of $[\text{Rh}(\text{PSPH-C}_2)_2]\text{BF}_4$ (0.05 M), $\text{CH}_3\text{SO}_3\text{H}$ (0.05 M), 2-hexanone (0.03 M) and (a) $^{18}\text{O}_2$ (99%) (1 atm), H_2O (0.1 M) or (b) O_2 (1 atm), $^{18}\text{OH}_2$ (18%) (0.1 M).

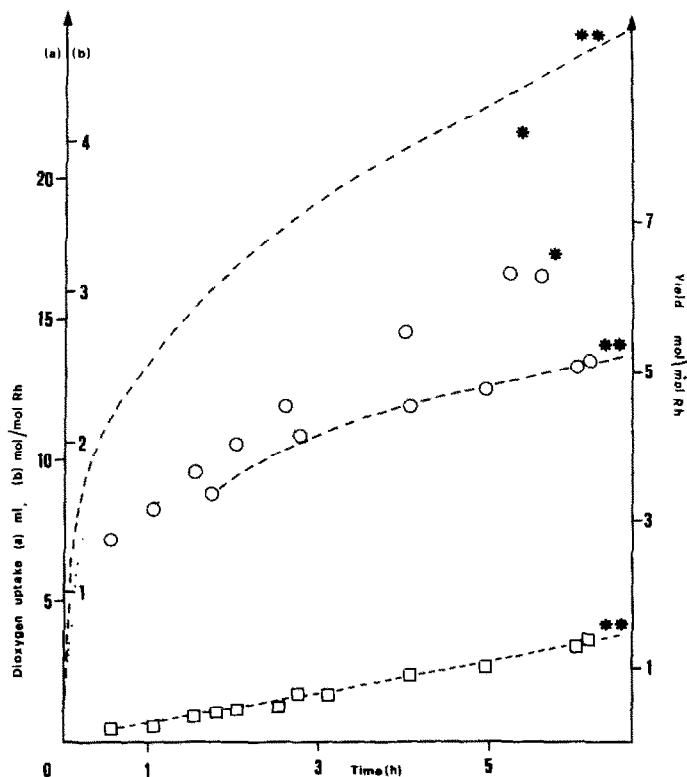


Fig. 4. Reaction profiles for the O_2 -oxidation of ($*$) ethanol to acetal ($\cdots\cdots\text{O}_2$ absorbed, $\circ\cdots\cdots\text{O}$ acetal formed); ($**$) ethanol to acetal and 1-octene (0.25 M) to 2-octanone ($\cdots\cdots\text{O}_2$ absorbed, $\circ\cdots\cdots\text{O}$ acetal formed, $\square\cdots\cdots\square$ 2-octanone formed) in the presence of $[\text{Rh}(\text{PSPH-C}_2)_2]\text{BF}_4$ (0.01 M), $\text{CH}_3\text{SO}_3\text{H}$ (0.01 M), T 50°C and $P(\text{O}_2)$ 1 atm.

suggested by Nyberg et al. [20] for related rhodium-promoted oxidation reactions. However, the fact that in our case the oxidation (although non-catalytic) of the organic substrate takes place even in the absence of an oxidizable alcohol, seems to rule out the hydrogen peroxide route. On the other hand (Fig. 4), oxidation of the olefin apparently competes with that of the alcohol and less acetal is produced in the presence of the olefin. This may indicate that the metal center is involved in both catalytic processes and that, if the hydrogen peroxide route is operating, the H_2O_2 produced never leaves the coordination sphere of the metal.

A final remark deals with the role of the acid. Stoichiometric oxygen transfer is also possible in the absence of added acid (see Fig. 2), but it appears to be necessary for the oxidation to become catalytic. Thus, as shown in Scheme 1, the acid does play an essential role in the transfer of the second oxygen atom to the alcohol, rather than in the formation of the methyl ketone.

Acknowledgement

We thank Mr. A. Ravazzolo for technical assistance.

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