was complete, decomposition to form pale green (platinum(II)) or deep red (palladium(II)) solutions indicated the formation of colloidal metal. The observation of this decomposition raised the question as to whether it was colloidal metal or the metal complex that was the active catalyst. An attempt to resolve this by vigorously stirring a solution with metallic mercury to suppress the catalytic activity of the metallic platinum present[33] certainly had no influence on the rate of reaction, strongly suggesting that it was the metal complexes that were the active species.

Although hydrogenation was not apparent under 1 atm of hydrogen, it did take place at higher pressures. In the case of the palladium(II) bis(acetone) complexes, very rapid oct-1-ene isomerization took place at higher hydrogen pressures, followed by slow hydrogenation accompanied by extensive decomposition and precipitation of metallic palladium. In the case of the platinum(II) bis(acetone) complexes, the rate of hydrogenation at higher hydrogen pressures was enhanced so as to be comparable to the isomerization rate. In contrast to the case with isomerization reported above, the dppe platinum complex was more effective than its $PMePh_2$ analogue in promoting hydrogenation, although there was no significant difference between the palladium complexes. As in the case of the palladium system, decomposition to metallic platinum was observed.

The behavior of $[Pd_2(\mu\text{-}Cl)_2(PMePh_2)_4](ClO_4)_2$ at higher hydrogen pressures was noteworthy. For the first period of the reaction the solutions remained yellow and appeared unchanged. However, after about 20 h a deep red color was observed, while GC analysis showed the formation of significant quantities of octane. The deep red solutions were insensitive to light and could be stored under a nitrogen atmosphere for several days without change. On exposure to air, the deep red solution returned to its original yellow color and no metallic palladium was precipitated. In the absence of oct-1-ene, a solution of $[Pd_2(\mu\text{-}Cl)_2(PMePh_2)_4](ClO_4)_2$ in 1:1 dichloromethane/acetone became slightly orange when exposed to 15 atm of hydrogen for 48 h at 25 °C. On the readmittance of air for a short period, the original yellow coloration was restored, and a small amount of metallic palladium was precipitated. These observations tend to suggest that the unidentified red species is stabilized by oct-1-ene. This red species is strongly reminiscent of the remarkable red palladium(I) complex $[Pd_2(dppe)_2](ClO_4)_2$ observed during the alcoholysis of silanes catalyzed by $[Pd(dppe)(ROH)_2](ClO_4)_2$.[10]

Acknowledgment. We thank the Petrochemicals and Plastics Division of ICI plc and the SERC for a CASE award (to A.W.) and Dr. R. Pearce for valuable discussions and help during the industrial phase of the studentship.

Registry No. $[Pd(PMePh_2)_2(py)_2](ClO_4)_2$, 118206-80-7; $[Pt(PMePh_2)_2(py)_2](ClO_4)_2$, 118206-82-9; $[Pd(PPh_3)_2(py)_2](ClO_4)_2$, 118206-84-1; $[Pt(PPh_3)_2(py)_2](ClO_4)_2$, 118245-51-5; $[Pd(PMePh_2)_2(dmso)_2](PF_6)_2$, 118206-86-3; $[Pt(PMePh_2)_2(dmso)_2](ClO_4)_2$, 118206-88-5; $[Pd(PPh_3)_2(dmso)_2](PF_6)_2$, 118206-90-9; $[Pt(PPh_3)_2(dmso)_2](PF_6)_2$, 118206-92-1; $[Pt(PPh_3)_2(dmso)_2](ClO_4)_2$, 118206-93-2; $[Pd(dppe)(Me_2CO)_2](ClO_4)_2$, 75845-46-4; $[Pt(dppe)(Me_2CO)_2](ClO_4)_2$, 118206-95-4; $[Pd(PMePh_2)_2(Me_2CO)_2](ClO_4)_2$, 118206-97-6; $[Pt(PMePh_2)_2(Me_2CO)_2](ClO_4)_2$, 118206-99-8; $[Pd(PPh_3)_2(Me_2CO)_2](ClO_4)_2$, 118226-08-7; $[Pd(OClO_3)(dppe)(Me_2CO)](ClO_4)$, 118207-01-5; $[Pd_2(\mu\text{-}Cl)_2(dppe)_2](ClO_4)_2$, 72476-84-7; $[Pd_2(\mu\text{-}Cl)_2(PMePh_2)_4](ClO_4)_2$, 118207-03-7; $[Pd_2(\mu\text{-}Cl)_2(dppe)_2](ClO_4)_2$, 73558-22-2; $[Pt_2(\mu\text{-}Cl)_2(dppe)_2](ClO_4)_2$, 118226-09-8; *cis*-$[PdCl_2(Ph_2PCH_2CH_2PPh_2)]$, 19978-61-1; *cis*-$[PdCl_2(PMePh_2)_2]$, 29484-75-1; *cis*-$[PtCl_2(Ph_2PCH_2CH_2PPh_2)]$, 14647-25-7; *cis*-$[PtCl_2(PMePh_2)_2]$, 16633-72-0; *cis*-$[PtCl_2(PPh_3)_2]$, 15604-36-1; *trans*-$[PdCl_2(PPh_3)_2]$, 28966-81-6; oct-1-ene, 111-66-0.

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Selective Oxidations of Olefins Catalyzed by Platinum(II) Complexes. Use of *tert*-Butyl Hydroperoxide and Potassium Caroate as Oxidants: Ketone vs Epoxide Formation

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Four low-cost oxidants have been tested in the oxidation of olefins catalyzed by either $[(diphoe)Pt(CF_3)(CH_2Cl_2)]BF_4$ or $(diphoe)Pt(CF_3)(OH)$ (diphoe = *cis*-1,2-bis(diphenylphosphino)ethylene) under mild conditions. These include sodium hypochlorite, sodium perborate, *tert*-butyl hydroperoxide, and potassium hydroperoxysulfate (caroate). While the first two are inactive, with the second two, selective ketonization of the olefin or selective epoxidation (including terminal olefins) can be obtained. A discussion is also included concerning the origin of selectivity in this class of catalysts based essentially on steric factors.

Introduction

Interest in the selective epoxidation of olefins with transition-metal complexes is still high since epoxides are very important building blocks in the petrochemical industry.[2]

We have recently reported[3,4] on a platinum(II) system that is able to catalyze very efficiently the selective epoxidation of simple terminal olefins with diluted (5–35%) hydrogen peroxide. Typical catalysts are complexes of the type $P_2Pt(CF_3)X$ (P_2 = diphosphine; X = solvent, –OH) that play a bifunctional role in the system (Scheme I) since (i) they activate otherwise unreactive olefins toward nucleophilic attack and (ii) they increase H_2O_2 nucleophilicity by forming Pt–OOH species through acid–base reactions. This system is highly chemoselective since epoxides are the only detectable oxidation products. Moreover, by modifying the catalysts with chiral diphosphines it has been possible to obtain also enantioselective epoxidation of simple olefins[5] with optical purities up to 41% in the case of propylene oxide.

Scheme I

olefin activation

$$Pt^+ + ol \rightleftharpoons Pt(ol)^+ \tag{1}$$

increase H_2O_2 nucleophilicity

$$Pt\text{–}OH + H_2O_2 \rightleftharpoons Pt\text{–}OOH \tag{2}$$

ol = olefin

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(1) (a) University of Venice. (b) University of Padua.

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Table I. Oxidation of Olefins with *t*-BuOOH in the Presence of either **2** or **1** as Catalyst[a]

					10^2[products], M			
					2 h		24 h	
run	catalyst	olefin	*T*, °C	solv	ketone	epoxide	ketone	epoxide
1	**2**	1-octene	20	CH_2Cl_2			0.33	0.12
2	**2**	1-octene	20	THF			0.16	
3[b]	**2**	1-octene	20	CH_2Cl_2	0.28		0.32	
4	**1**	1-octene	20	CH_2Cl_2	0.91	0.41	1.6	0.66
5	**1**	1-octene	83	DCE	6.2		7.3	
6	**1**	1-hexene	83	DCE	1.8		3.2	
7	**1**	styrene	83	DCE	5.1		25.6	
8	**1**	cyclohexene	83	DCE		*c*		
9	**1**	*cis*-4-methyl-2-pentene	83	DCE		*c*		
10	**1**	allyl methacrylate	83	DCE	2.8		4.6	
11	**1**	allyl alcohol	83	DCE		*c, d*		
12	**1**	allyl chloride	83	DCE		*c, d*		

[a] Experimental conditions: [Pt], 10^{-2} M; [olefin], 0.75 M; [*t*-BuOOH], 0.70 M; N_2, 1 atm. DCE = 1,2-dichloroethane. [b] H_2O added (H_2O/Pt = 70). [c] No reaction. [d] Decomposition to Pt metal is observed.

Because of the generality of reaction 2, this system appears to be potentially useful to exploit the reactivity of other primary oxidants that can react either with $[P_2Pt(CF_3)(solv)]^+$ or with $P_2Pt(CF_3)(OH)$. To this purpose we have directed our attention toward a series of low cost oxidants like sodium hypochlorite, sodium perborate, *tert*-butyl hydroperoxide and potassium hydroperoxysulfate (caroate). In this paper, we report the results obtained in the exploration of the reactivity of these oxidants toward a variety of simple olefins in the presence of our Pt(II) catalysts, which allow also for a discussion concerning the origin of selectivity in these oxidation reactions.

Results and Discussion

Sodium Hypochlorite and Sodium Perborate. While $NaBO_3$ has not found, to our knowledge, any use in transition-metal-mediated alkene oxidations, NaClO has been employed as a monooxygen donor for the formation of metal–oxo species either with metalloporphyrins for the oxidation of olefins and aromatics[6] or with transition-metal salts for the oxidation of alcohols, ethers, and aromatics.[7]

We have initially attempted to synthesize complexes of platinum(II) through the reaction

$$[(\text{diphoe})Pt(CF_3)(CH_2Cl_2)]^+ + {}^-OX \rightarrow (\text{diphoe})Pt(CF_3)(OX) \quad (3)$$

diphoe = *cis*-1,2-bis(diphenylphosphino)ethylene

X = Cl, BO_2

This has been carried out by stirring vigorously stoichiometric amounts of an aqueous solution of the oxidant with the cationic complex dissolved in CH_2Cl_2. While no reaction takes place with $NaBO_3$, with NaClO the reaction affords quantitative amounts of (diphoe)$Pt(CF_3)Cl$. The latter result seems to indicate the existence of an interaction between platinum and hypochlorite that might be of some interest for oxygen transfer if this is sufficiently fast.

Therefore, we have attempted to oxidize 1-octene with NaClO and $NaBO_3$ using as catalyst $[(\text{diphoe})Pt(CF_3)(CH_2Cl_2)](BF_4)$ (**1**) in a biphasic (CH_2Cl_2/H_2O) medium. Unfortunately no reaction takes place, since with NaClO the catalyst rapidly deactivates to form the corresponding chloride, while with $NaBO_3$ no oxidation product is observed even in the presence of phase-transfer agents (tetraethylammonium *p*-toluenesulfonate, tetrabutylammonium hydrogen sulfate) to increase the concentration of oxidant in the organic phase.

***tert*-Butyl Hydroperoxide.** On the use of *t*-BuOOH as oxidants for organic substrates, a rapidly expanding literature has been growing since the commercialization of the Oxirane process.[8]

This reactant has been widely used in this laboratory in the synthesis of a variety of *tert*-butyl peroxo complexes of Pt(II)[9] according to the reaction

$$P_2Pt(Rx)(OH) + t\text{-BuOOH} \rightarrow P_2Pt(Rx)(OO\text{-}t\text{-Bu}) + H_2O \quad (4)$$

P_2 = two monophosphines or one diphosphine

Rx = substituted alkyl or aryl

In this work we have tested *t*-BuOOH in catalytic oxidations using either **1** or (diphoe)$Pt(CF_3)(OH)$ (**2**) under different experimental conditions. The results obtained are summarized in Table I, where the products formed after 2 and 24 h are reported. As shown we have initially tried to determine the most appropriate conditions for the reaction using 1-octene. The use of **2** as catalyst at room temperature (runs 1–3) gives rather poor results; the reaction is always less than stoichiometric independent of the solvent or the presence of water, which is known[4] to be important in increasing the ionic character of the Pt–O bond of the hydroxo complex, thereby promoting the creation of a vacant coordination site for the olefin.

The results are more interesting when **1** is used as catalyst either under the same experimental conditions (run 4) or by increasing the reaction temperature to 83 °C (run 5). Under these experimental conditions the selectivity of the reaction is much better since 1,2-epoxyoctane formation is suppressed and 2-octanone is the exclusive oxidation product. This behavior is confirmed when other olefins are used. It can also be observed that the system is reactive toward simple terminal olefins (runs 5–7), while it is inert with respect to internal olefins (runs 8, 9), thereby confirming some previous data obtained with *tert*-butylperoxo complexes of trans geometry.[9] Moreover, with respect to a series of allyl derivatives, only allyl methacrylate is oxidized to give 2-ketopropyl methacrylate selectively (the methacrylic double bond cannot be ketonized), while in the presence of allyl alcohol or allyl chloride, the catalyst rapidly (about 2 h) decomposes to Pt metal.

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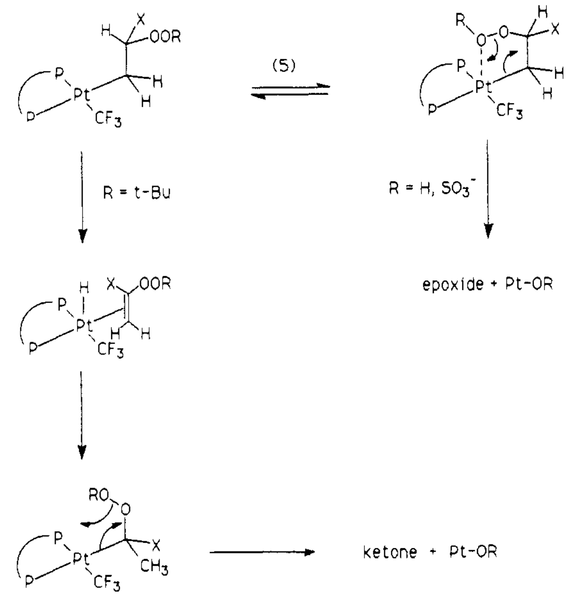
Scheme II



Origin of Selectivity. These results offer some interesting insights into the origin of selectivity in the oxidation of olefins with systems of the type hydroperoxide/groups 8–10 transition metal. We have recently suggested[4,10] for the selective epoxidation of olefins with H_2O_2 in the presence of the same class of complexes of Pt(II) that, after the transfer of the peroxidic moiety onto the coordinated olefin, the evolution of the intermediate species to products (Scheme II) is controlled basically by the position of the configurational equilibrium 5 (open-chain vs cyclic). The results here reported for *t*-BuOOH (selective ketonization) compared to those obtained with H_2O_2 (selective epoxidation) provide clear-cut evidence for this view and show that the control on selectivity in this system is essentially steric as is implied in equilibrium 5. In fact, when R = *t*-Bu (Scheme II), the closure of the ring from the axial position becomes an unfavored process, since the bulky *t*-Bu group cannot easily slide between the phenyl substituents of the *cis*-diphosphine ligand, as is clearly indicated by molecular models. However, while this argument may be sufficient to explain the observed complete selectivity to ketones at 80 °C when *t*-BuOOH is used as the oxidant, the >99% selectivity to epoxides observed with H_2O_2 or $KHSO_5$ (vide infra), which in principle could proceed either way in Scheme II because of lack of sterical constraints, needs some additional conditions. These are (i) a relatively difficult β-hydride elimination–addition and (ii) a stable, 5-coordinate platinum intermediate of the type P_2(olefin)Pt(CF_3)(H) (Scheme II), to prevent further reaction. This view seems to be supported by a number of experimental observations.

The temperature effect on selectivity reported in Table I suggests that the β-hydride elimination–addition, which is required for the formation of ketones and is a sort of one-way path for R = *t*-Bu, is, for the present class of complexes, a relatively difficult pathway, which is favored at higher temperatures.

In an attempt to increase the catalytic activity of the system, we have used a bimetallic Pd/Pt mixture as catalyst since it is known that Pd complexes activate olefins toward nucleophilic attack more efficiently than Pt complexes. Therefore, [(dppe)Pd(CF_3)(CH_2Cl_2)]BF_4[9] (2×10^{-3} M) (dppe = 1,2-bis(diphenylphosphino)ethane) as olefin activator was associated with (diphoe)Pt(CF_3)(OH) (2×10^{-3} M) as H_2O_2 activator in the oxidation of 1-octene at 20 °C with 17% H_2O_2 as the oxidant. The initial rate (1.2×10^{-5} M s^{-1}) observed was comparable to that obtained with platinum alone, while palladium alone was inactive under the same experimental conditions. Interestingly, only 2-octanone was selectively produced, indicating that when Pt is substituted by Pd in Scheme II, the β-hydride elimination–addition pathway becomes overriding.

As to the stability of the above mentioned 5-coordinate intermediate, which is a hydrido trifluoromethyl species, we have observed that (diphosphine)platinum–methyl and –phenyl derivatives rapidly decompose to Pt(0) under catalysis conditions,[4] while $P_2Pt(CF_3)X$ catalysts (X = solvent, –OH), where P_2 is a wide variety of (tetraphenyldiphosphino)alkane ligands, have all proved active and stable in the epoxidation of 1-octene with 17% H_2O_2.[11] Interestingly, $P_2Pt(CF_3)H$ complexes (P_2 = *cis*-1,2-bis(diphenylphosphino)ethylene, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, 1,2-bis(dimethylphosphino)ethane) have been synthesized and have proved stable toward reductive elimination at room temperature,[12] while the CH_3 and Ph derivatives have not.[13] However, [(dmpe)Pt(CF_3)(CH_2Cl_2)]BF_4 (dmpe = 1,2-bis(dimethylphosphino)ethane) in the same catalytic oxidation rapidly undergoes reductive elimination to produce a Pt(0) species. This result seems to suggest that some alternative pathway is available to this complex, probably oxidative addition of Pt(II) → Pt(IV) by H_2O_2 or even CH_2Cl_2,[12,14] followed by reductive elimination, due to the increase in the nucleophilicity of the metal promoted by the more basic diphosphine.

In general, when considering also other metals like Rh,[15] Ir,[16] and Pd[17] for which the chemistry described in Scheme II is very likely involved, we suggest that in the oxidation of olefins with hydroperoxides the selectivity (ketone vs epoxide) of the system is controlled essentially by two factors: (*i*) the influence of steric hindrance on equilibrium 5; (*ii*) the ease with which the individual metal center can promote β-hydride elimination–addition. Of groups 8–10 transition metals only Pt appears to meet the appropriate balance of these two factors to produce epoxides; for all the other metals the tendency to promote β-hydride addition–elimination seems overriding, with the exception of some metal–nitro complexes, for which the same chemistry shown in Scheme II was originally suggested,[18] where some selectivity toward epoxidation has been observed in the case of very rigid olefinic systems.[19]

Potassium Hydroperoxysulfate. Potassium hydroperoxysulfate (hereafter caroate) is a hydroperoxidic oxidant the nature of which has been definitely assessed only recently through X-ray analysis.[20] Its use as epoxidizing agent has been reported in recent years in purely organic systems where the actual oxidant is a dioxirane transient species, generated in situ by reaction of caroate with ketones added as catalysts.[21] The only example of metal-catalyzed

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Table II. Epoxidation with 1-Octene with Caroate under Different Experimental Conditions[a]

run	catalyst	olefin/Pt	Caroate/Pt	[caroate],[b] M	10^2[epoxide formed], M		% caroate dec[c]
					2 h	24 h	
1	**1**	45	26	0.8	5.1	8.0	39
2	**1**	45	130	0.86	0.2	0.7	93
3	**1**	93	46	0.92	2.5	4.1	52
4	**1**	45	68	0.085	4.9	13.4	8
5	**2**	45	26	0.86	10.8	14.5	9
6	**2**	45	15	0.085	14.6	25.4	0.2

[a] Experimental conditions: [Pt], 1.9 × 10^{-2} M; solvent, CH_2Cl_2/H_2O; N_2, 1 atm; *T*, 20 °C. [b] Concentration of the aqueous solution used. [c] Determined by titration of the residual caroate after 24 h.

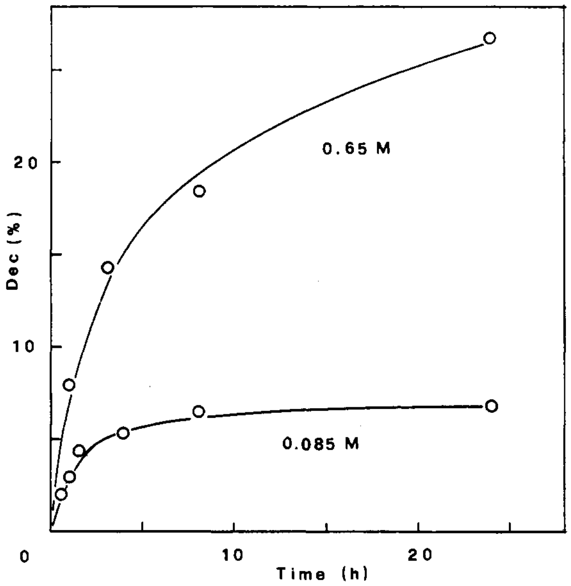

Figure 1. Decomposition of caroate in the presence of **1** at room temperature. [Pt] = 1.8 × 10^{-2} M in CH_2Cl_2; caroate/Pt = 68. Numbers on the curves refer to the concentrations of the caroate aqueous solutions.

oxidation with caroate is due to Meunier and co-workers for the epoxidation of olefins or the hydroxylation of aromatics via metal–oxo formation on a series of manganese porphyrins.[22]

Caroate is commercially available with the trade name of Oxone, which is a 2/1/1 mixture of $KHSO_5$, $KHSO_4$, and K_2SO_4 and therefore is strongly acidic in solution. For this reason a common feature of all the previous reports on oxidation reactions is the use of caroate water solutions buffered around pH 7. Under these experimental conditions, part of the oxidant is always lost because of autodecomposition reactions, which reach a maximum rate of pH values around the pK_a of caroate (9.3 at 25 °C in H_2O).[23]

We have tested our catalysts **1** and **2** dissolved in CH_2Cl_2 in the catalytic oxidation of 1-octene using simple water solutions of the commercial Oxone mixture without buffering. The only oxidation product obtained is 1,2-epoxyoctane. Initially the most appropriate conditions for the reaction were searched out, and a summary of the results obtained under the various operating conditions is reported in Table II. As shown in most cases the dominant factor is the percentage of oxidant that is wasted during the course of the reaction because of decomposition. This appears to depend on the absolute amount of caroate used and most of all on the concentration of the aqueous solution employed. These losses of caroate can be explained by noting that the Pt complex catalyzes the decomposition of $KHSO_5$, as is known for a variety of metal ions.[23] Moreover, we know from past experience that this class of Pt complexes are able to catalyze the decomposition of peroxy acids like *m*-chloroperbenzoic acid.[9]

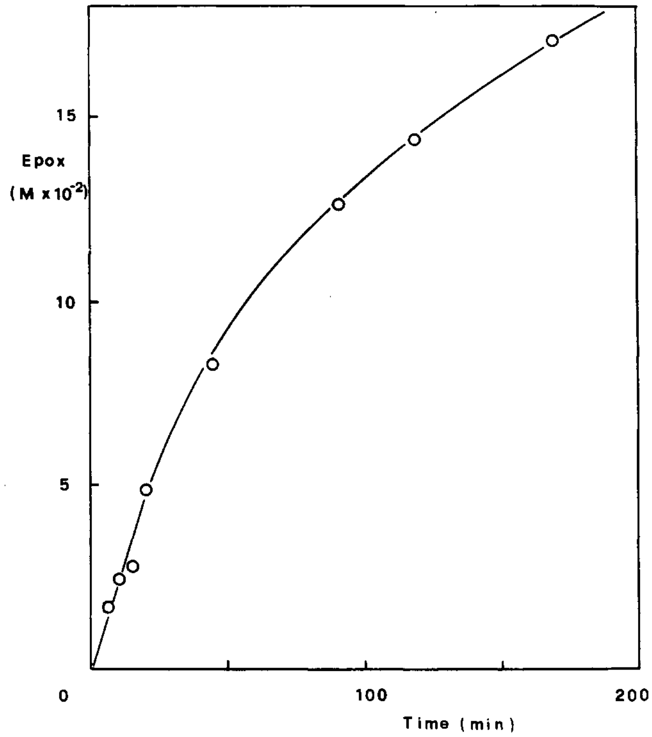

Figure 2. Reaction profile for the catalytic epoxidation of 1-octene with caroate in the presence of **2** as catalyst (Table III, run 2).

Table III. Epoxidation of Different Olefins with Caroate Catalyzed by **2**[a]

run	olefin	10^2[epoxide formed], M		
		2 h	5 h	24 h
1	1-hexene	7.4	10.5	13.0
2	1-octene	14.4	20.0	25.1
3	propylene[b]	8.3	12.0	17.5
4	styrene			
5	cyclooctene[c]	2.5 (1.3)	5.1 (2.4)	12.9 (8.1)
6	*cis*-4-methyl-2-pentene	2.2	5.1	9.2
7	allylbenzene[d]	0	0.4	3.2
8	allyl chloride[d]	1.8	7.2	13.2

[a] Experimental conditions: [Pt], 1.8 × 10^{-2} M; [olefin], 0.81 M; [caroate], 0.085 M, caroate/Pt = 15; solvent, CH_2Cl_2/H_2O; *T*, 20 °C; N_2, 1 atm. [b] Propylene at 1 atm. [c] Numbers in parentheses refer to blank reactions carried out without Pt. [d] Solvent is DCE.

We have carried out a test experiment (Figure 1) where a solution of **1** in CH_2Cl_2 was stirred with two aqueous solutions of caroate at different concentrations but the ratio caroate/platinum was kept constant. The aqueous layer was periodically sampled (0.5 mL) and titrated iodometrically to determine the percent decomposition. As is clear from Figure 1, the solution at lower concentration is much more stable although, even in this case, some decomposition is evident. However, it has to be pointed out that aqueous solutions of caroate <0.1 M can be stored for weeks in the refrigerator without appreciable loss of concentration.

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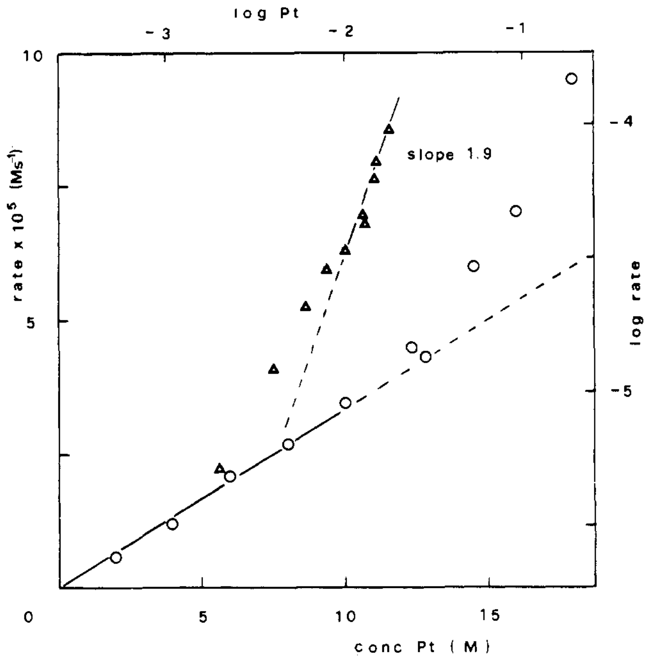

Figure 3. Effect of the concentration of **2** in the catalytic epoxidation of 1-octene with caroate: circles, linear plot; triangles, log–log plot. Experimental conditions: [1-octene], 0.66 M in CH_2Cl_2; [caroate], 0.085M in H_2O; caroate/1-octene (mole ratio) = 1.64; solvent, CH_2Cl_2/H_2O; T, 20 °C.

In the search for the best operating conditions we have also used phase-transfer agents (tetraethylammonium *p*-toluenesulfonate, tetrabutylammonium hydrogen sulfate), the influence of which under the same conditions as run 1 is negligible. It has to be noted that the use of complex **2** instead of **1** as catalyst increases significantly the amount of epoxide formed while decreasing the decomposition of the oxidant.

On the basis of these results we have studied the epoxidation of various olefins with **2** as catalyst with caroate in diluted solutions (<0.1 M). In Figure 2 we report a typical reaction profile, while in Table III the amounts of epoxide formed in the individual cases after 2, 5, and 24 h are shown. At variance with results for the use of H_2O_2,[3] with caroate it is possible to accomplish the epoxidation of internal olefins (runs 5 and 6) and also of some allyl derivatives. Moreover, when allyl alcohol is reacted under experimental condition as in Table III, the oxidation is completed in less than 2 h. However, no epoxide can be observed since, as the latter is completely soluble in H_2O, only products arising from oxirane ring opening can be detected. Conversely, despite the use of a strongly acidic solution of the oxidant, no evidence for acid hydrolysis of the epoxides was ever found in all the cases reported in Table III.

Since it is known[24] that some water-insoluble olefins can be epoxidized with caroate alone in the presence of MeOH, we have carried out some blank reactions without platinum for all the olefins reported in Table III. The amounts of oxidation products obtained under these experimental conditions were negligible with the exception of cyclooctene for which significant Pt-independent epoxidation was observed.

In the case of H_2O_2 as the oxidant,[10] we have studied the system kinetically in the epoxidation of 1-octene where a second-order dependence on platinum concentration was observed. Unfortunately, in this case a complete analysis is impossible because of the partial decomposition of caroate when its concentration is increased. However, we have thought it useful to determine the influence of the concentration of platinum on the initial rates in order to have some insights on the mechanistic aspects of the epoxidation reaction. The results are shown in Figure 3 and bear close similarities to previous findings on the same system where H_2O_2 is used instead. In fact significant deviation from linearity is evident for Pt concentration higher than 10^{-2} M and the log–log plot clearly indicates a second-order dependence under these experimental conditions. Unfortunately the Pt concentration cannot be increased over 1.8×10^{-2} M since for rates higher than 10^{-4} M s^{-1} the reaction is controlled by the diffusion of the oxidant from the aqueous to the organic phase. Therefore, we infer that the reaction pathway involved will be similar to that with H_2O_2[10] (Scheme III). Reaction 7 has been included to account for the observed higher activity of **2** with respect to **1**. It is in fact known[10] that in the presence of acids $[(diphoe)Pt(CF_3)(H_2O)]^+$ forms from $(diphoe)Pt(CF_3)(OH)$ and that 1-octene displaces coordinated H_2O more easily than HO^-. This leads to a more favorable balance between $Pt(ol)^+$ and PtOOS in reaction 9.

Scheme III

$$\mathrm{PtOH + HOOS \rightleftharpoons PtOOS + H_2O} \qquad (6)$$

$$\mathrm{PtOH + H^+ \rightleftharpoons Pt(H_2O)^+} \qquad (7)$$

$$\mathrm{Pt(H_2O)^+ + ol \rightleftharpoons Pt(ol)^+ + H_2O} \qquad (8)$$

$$\mathrm{Pt(ol)^+ + PtOOS \rightarrow epoxide + Pt^+ + PtOS} \qquad (9)$$

$$\mathrm{ol = 1\text{-}octene;\ S = SO_3^-}$$

The observed second-order dependence on Pt at higher concentrations is strong evidence that, under certain experimental conditions, the actual oxidant in the catalytic system can be a metal-containing species. From the chemistry known for this class of complexes, we suggest that this may well be a platinum(II) peroxysulfate complex formed according to reaction 6 from the weak base **2** and the weak acid HSO_5^-. We have tried to see the peroxo species with ^{19}F NMR spectroscopy by adding an excess of Oxone dissolved in water to **2** in CD_2Cl_2. The spectrum of the mixture showed a decrase of the signals typical of **2**,[10] the appearance of two large bands attributable to **1**,[10] and a new species (about 30%) centered at δ −23.58 dd ($^3J_{F-P_{cis}}$ = 12.2 Hz, $^3J_{F-P_{trans}}$ = 59.3 Hz, $^2J_{F-Pt}$ = 569 Hz), which could be the PtOOS species of Scheme III as a consequence of a deshielding of the CF_3 signal due to the adjacent SO_3^- group. It has to be pointed out that attempts to synthesize the $(diphoe)Pt(CF_3)(OOSO_3^-K^+)$ species from the corresponding PtOH and the commercial Oxone resulted only in the formation of a mixture containing about 40% of the final product and about 60% of the starting hydroxo complex (^{19}F NMR evidence). This material shows a strong IR band at 1270 cm^{-1} that closely resembles the S=O stretching vibration of the persulfate anion.[25] The 40% peroxidic nature of this material was confirmed by iodometric titration.

The evidence for the existence of the PtOOS species may provide also a rationale to explain the above-reported decomposition of caroate promoted by platinum; in other words, PtOOS may well be both the oxidant for the catalytic reaction and the species from which the decomposition of caroate initiates.

The selectivity observed in the epoxidation reaction leads again to Scheme II as the most likely chemistry involved in the course of reaction 9 and hence to a selectivity, epoxide vs ketone, based essentially on steric grounds. From this point of view it is interesting to notice that using *always the same catalysts* (i.e. **1** or **2**) in the oxidation of olefins, one can obtain cleanly the desired product by simply choosing the appropriate oxidant: terminal epoxides (with H_2O_2), terminal ketones (with *t*-BuOOH), internal epoxides (with $KHSO_5$).

Experimental Section

Apparatus. IR spectra in Nujol mulls were recorded on a Perkin-Elmer 683 spectrophotometer using CsI plates. GLC measurements were taken on a Hewlett-Packard 5890A gas chromatograph, equipped with a flame-ionization detector and a Hewlett-Packard 3390A electronic integrator. Identification of products was made with GLC by comparison with authentic samples.

Materials. Solvents were dried and purified according to standard methods. Commercial olefins were purified by passing them through

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neutral alumina and were distilled and stored under N_2 in the dark. The oxidants, 10% NaClO in H_2O (Carlo Erba), $Na_2BO_3{\cdot}4H_2O$ (Fluka), 80% *tert*-butyl hydroperoxide (Fluka) and Oxone (Janssen) were commercial products and used without purification. Where necessary the solutions containing the oxidants were titrated iodometrically. Where not available commercially, the epoxide products were prepared by literature procedure.[26] The catalysts $[(diphoe)Pt(CF_3)(CH_2Cl_2)](BF_4)$ and (diphoe)-$Pt(CF_3)(OH)$ were prepared according to already described methods.[26] The dmpe derivatives were prepared from $(PPh_3)_2Pt(CF_3)Cl$[27] according to the following procedure.

(dmpe)Pt(CF$_3$)Cl. To a suspension of *trans*-$(PPh_3)_2Pt(CF_3)Cl$ (0.40 g, 0.48 mmol) in THF (20 mL) was added in one portion dmpe (0.075 g, 0.50 mmol), and the reaction mixture was stirred at room temperature for 2 days. After this time a white solid formed. The solution was concentrated under reduced pressure to about 10 mL. The solid was filtered off, washed with *n*-pentane (3 × 2 mL), and dried in vacuo. Yield: 60%. Anal. Calcd (found): C, 18.70 (18.75); H, 3.59 (3.62). IR (Nujol): 279 cm^{-1} (Pt–Cl). ^{19}F NMR (CD_2Cl_2): δ −25.50, (dd), $^3J_{FP_{cis}} = 10.0$ Hz, $^3J_{FP_{trans}} = 58.2$ Hz, $^2J_{FPt} = 566$ Hz. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 29.0 (dq, trans CF_3), $^3J_{PF} = 58.2$ Hz, $^2J_{PP} = 3.7$ Hz, $^1J_{PPt} = 1825$ Hz; δ 23.1 (dq, cis CF_3), $^3J_{PF} = 10.0$ Hz, $^2J_{PP} = 3.7$ Hz, $^1J_{PPt} = 3745$ Hz.

(dmpe)Pt(CF$_3$)(CH$_2$Cl$_2$)BF$_4$. $(dmpe)Pt(CF_3)Cl$ (0.30 g, 0.67 mmol) was dissolved in CH_2Cl_2 (20 mL), and the solution was carefully degassed. A 0.68-mL aliquot of a 1 M solution of $AgBF_4$ in acetone was added dropwise. The mixture was stirred for 1 h, AgCl was filtered off, and the filtrate was brought to dryness in vacuo. The white solid obtained is very hygroscopic and can be stored under a dry N_2 atmosphere. Yield: 95%. Anal. Calcd (found): C, 16.40 (16.31); H, 3.10 (3.14).

Catalytic Reactions. These were carried out in a 25- or 50-mL round-bottomed flask equipped with a stopcock for vacuum/N_2 operations and a side-arm fitted with a screw-capped silicone septum to allow sampling. Constant temperature (25 °C) was maintained by water circulation through an external jacket connected with a thermostat. For reactions at 83 °C the reactors were unjacketed to allow heating through an external oil bath and equipped with a reflux condenser. Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer.

Absence of diffusional problems below 1.0×10^{-4} M s^{-1} initial rates was determined by the independence of conversion vs time plots on the stirring rate on experiments randomly selected from Figure 3.

The general procedure here reported was followed in all cases. In a typical experiment the appropriate amount of solid catalyst was placed in the reactor, which was evacuated and placed under N_2 atmosphere. Dry, N_2-saturated CH_2Cl_2 was added, followed by 1-octene. After a few minutes of stirring, the oxidant solution was injected and the time was started. In reactions carried out at 83 °C, DCE was used as solvent instead of CH_2Cl_2, and after the usual procedure, the reaction mixture was rapidly brought to reflux. The conversion was monitored by sampling periodically the reaction mixture with a microsyringe.

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Registry No. **1**, 98839-55-5; **2**, 70504-87-9; dmpe, 23936-60-9; *trans*-$(PPh_3)_2Pt(CF_3)Cl$, 71581-10-7; $(dmpe)Pt(CF_3)Cl$, 118017-52-0; $(dmpe)Pt(CF_3)(CH_2Cl_2)BF_4$, 118017-54-2; *tert*-butyl hydroperoxide, 75-91-2; potassium hydroperoxysulfate, 10058-23-8; 1-octene, 111-66-0; 1-hexene, 592-41-6; styrene, 100-42-5; *cis*-4-methyl-2-pentene, 691-38-3; allyl methacrylate, 96-05-9; allyl chloride, 107-05-1; propylene, 115-07-1; cyclooctene, 931-88-4; allylbenzene, 300-57-2; sodium hypochlorite, 7681-52-9; sodium perborate, 7632-04-4.

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Effects of Replacing Oxygen by Sulfur at the Endogenous Bridging Center on the Redox Properties of Binuclear Copper(II) Complexes

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The comparative voltammetry of the binuclear complexes $L(O)Cu_2(pz)$ and $L(S)Cu_2(pz)$ at mercury, platinum, gold, and glassy-carbon electrodes in dichloromethane, tetrahydrofuran, dimethylformamide, and propyl cyanide has enabled the influence of the endogenous bridging center on the redox properties to be examined in detail when oxygen (O) is replaced by sulfur (S). Each of the complexes exhibits an extended one-electron-transfer series:

$$L(X)Cu_2(pz) \overset{\text{process I}}{\underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}} [L(X)Cu_2(pz)]^- \overset{\text{process II}}{\underset{-e^-}{\overset{+e}{\rightleftharpoons}}} [L(X)Cu_2(pz)]^{2-}$$

$$L(X)Cu_2(pz) \overset{\text{process III}}{\underset{+e^-}{\overset{-e^-}{\rightleftharpoons}}} [L(X)Cu_2(pz)]^+ \overset{\text{process IV}}{\underset{+e^-}{\overset{-e^-}{\rightleftharpoons}}} [L(X)Cu_2(pz)]^{2+}$$

$X = O, S$; $L(X)^{3-}$ = binucleating ligand component; pz = pyrazolate bridge

In the noncoordinating solvent dichloromethane, reduction processes I and II for $L(O)Cu_2(pz)$ are well separated but are electrolyte- and electrode-dependent. With $L(S)Cu_2(pz)$, although the first reduction process occurs at a more negative potential than is the case with the oxygen analogue, the separation between processes I and II is significantly less. In dichloromethane, $[L(X)Cu_2(pz)]^{2-}$ is not stable even on the voltammetric time scale. However, in more polar solvents, nonspecific solvent terms provide increased stability. In contrast to the large separation in reduction process I and II, oxidation processes III and IV are not resolved in dichloromethane with $L(O)Cu_2(pz)$ and barely resolved for $L(S)Cu_2(pz)$, with the sulfur-bridged species being easier to oxidize than the oxygen-bridged complex. In polar coordinating solvents, the separation in the two oxidation potentials is increased. However, the stability of $[L(X)Cu_2(pz)]^+$ and $[L(X)Cu_2(pz)]^{2+}$ is decreased significantly by solvent-specific terms.

Introduction

The redox properties of binuclear copper complexes, Cu_2L, have received much attention in recent years, particularly with respect to studies endeavoring to understand and mimic the redox function of copper proteins.[4] The nature of the coordination environment of the copper is important in determining the redox properties. Oxygen, nitrogen, and sulfur centers have all been considered as

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