

Catalytic Epoxidation of 1-Octene with Diluted Hydrogen Peroxide: On the Basic Role of Hydroxo Complexes of Platinum(II) and Related Species[†]

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Abstract: The basic behavior of $P_2Pt(Rx)(OH)$ complexes (P_2 = two *tert*-monophosphines or -diphosphine; Rx = activated alkyl or aryl) has been investigated in protic media with pH and conductivity measurements. More insight into the nature of the Pt-O bond in diphosphine complexes has been gained with the aid of ^{31}P NMR from $^1J_{P-Pt}$ data. A wide class of cis and trans complexes of the above type has been tested as catalysts in the selective epoxidation of 1-octene with 35% H_2O_2 . Only diphosphine derivatives were found active. The system has been investigated both in monophasic (THF and EtOH) and biphasic (CH_2Cl_2/H_2O) media. The effect of cationic complexes and the dilution of H_2O_2 down to 5% are also reported. Evidence for the involvement of cationic platinum-olefin species in the catalytic cycle is reported, while the possible pathways with which oxygen transfer occurs are discussed in more detail, and a possible explanation is given for the unusual selectivity.

Introduction

The oxidation of olefins with transition-metal species has remained a primary goal during the years, since epoxides are very important building blocks in the petrochemical industry. The use of H_2O_2 as the oxidizing agent for this reaction was first reported by Milas et al.² about 50 years ago for the production of glycols. As it was later found, the process proceeds via epoxides that are rapidly hydrolyzed under the acidic conditions employed. To date, epoxidation with hydrogen peroxide suffers from several limitations which discourage the use for commercial operations: (i) it is useful for functionalized, rather reactive olefins; (ii) highly concentrated solutions of H_2O_2 are generally involved, with consequent safety problems; (iii) polar coordinating solvents are necessary which reduce strongly the transfer of oxygen to the hydrophobic olefin; and (iv) rather forcing conditions are employed which result in byproduct formation.³

From a mechanistic point of view, the use of early transition metals in their higher oxidation states (acidic metal centers) with substituted, relatively electron-rich olefins has led to the conclusion that oxygen transfer, in analogy with organic peroxyacids,⁴ proceeds in most cases via nucleophilic attack of the olefin on the electron-poor peroxidic oxygen.⁵ On the other hand, the use of basic metal centers has met with little success, to date, in the epoxidation of olefins, since covalent peroxo species of groups 8-10 transition metals in their lower oxidation states have led almost invariably to ketonization. In this case, a common mechanistic feature has been suggested to be the existence of a peroxy-metallocycle as the key reaction intermediate, formed from interaction of the organic substrate and the peroxo moiety at the same metal center.⁶

It has long been known that certain α - β unsaturated ketones or aldehydes or other electronegatively substituted olefins can be easily epoxidized with hydrogen peroxide under basic conditions (NaOH),⁷ the crucial feature being the nucleophilic addition of the hydroperoxide anion to the carbon-carbon double bond promoted by the electron-withdrawing substituent. Thus, in principle, one could use groups 8-10 transition-metal hydroxo species to fulfill the two requirements of the above-cited reaction with the advantage of having only one center capable of activating any olefin toward nucleophilic attack and producing hydroperoxide anions through acid-base reaction with HO^- .

Among the groups 8-10 M-OH species, those of platinum are by far the most stable and well-characterized complexes, the

number of which has been rapidly growing in the past few years.⁸⁻¹⁴ We have reported the synthesis and characterization of a wide class of hydroxo complexes of platinum(II) of the type $P_2Pt(Rx)(OH)$ ¹²⁻¹⁴ (P_2 = two monophosphines or diphosphine; Rx = substituted alkyl or aryl). Typically, these compounds undergo insertion reactions with SO_2 , CO, COS, CS_2 ,¹² CO_2 ,¹⁵ and RNC¹⁶ and acid-base reactions with weak sulfur, nitrogen, carbon acids,¹² and, significantly to the purpose of this study, with hydrogen peroxide^{14,17} and *tert*-butyl hydroperoxide^{14,18} to yield the corresponding peroxo complexes. The *tert*-butyl peroxo complexes have proved useful reagents for the oxidation of terminal olefins to methyl ketones under anhydrous conditions.¹⁴ Conversely, in protic media, the selective epoxidation of terminal olefins with H_2O_2 by (diphoe)Pt(CF₃)(OH) (diphoe = 1,2-bis(diphenyl phosphino)ethylene) has been reported by us in a preliminary account of this paper.¹⁹ The results obtained seemed to support

(1) (a) Università di Venezia. (b) Centro CNR.

(2) Milas, N.; Sussman, S. *J. Am. Chem. Soc.* **1936**, *58*, 1302. Milas, N.; Sussman, S. *Ibid.* **1937**, *59*, 2345. Milas, N. *Ibid.* **1937**, *59*, 2342.

(3) For a comprehensive review on this point, see: Sheldon, R. A. *Aspects Hom. Catal.* **1981**, *4*, 3.

(4) Bartlett, P. D. *Rec. Chem. Prog.* **1957**, *18*, 111.

(5) Sheldon, R. A.; Kochi, J. K. *Adv. Catal.* **1976**, *25*, 272 and references therein.

(6) Mimoun, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 734 and references therein.

(7) Plesnicar B. In "Oxidation in Organic Chemistry"; Trahanovsky, W. S.; Ed.; Academic Press: New York, 1978; Part C, p 211 and references therein.

(8) Bushnell, G. W.; Dixon, K. R.; Hunter, R. G.; McFarland, J. J. *Can. J. Chem.* **1972**, *50*, 3694.

(9) Phillips, D. A.; Kubota, M.; Thomas, J. *Inorg. Chem.* **1976**, *15*, 118.

(10) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993.

(11) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750. Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Yoshida, T. *Ibid.* **1973**, *95*, 3028.

(12) Michelin, R. A.; Napoli, M.; Ros, R. *J. Organomet. Chem.* **1979**, *175*, 239.

(13) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119.

(14) Strukul, G.; Michelin, R. A.; Orbell, J. D.; Randaccio, L. *Inorg. Chem.* **1983**, *22*, 3706.

(15) Michelin, R. A.; Strukul, G.; Bresciani-Pahor, N.; Zangrando, E.; Randaccio, L. *Inorg. Chim. Acta* **1984**, *84*, 229.

(16) Michelin, R. A.; Ros, R. *J. Organomet. Chem.* **1979**, *169*, C42.

(17) Michelin, R. A.; Ros, R.; Strukul, G. *Inorg. Chim. Acta* **1979**, *37*, L491.

(18) Strukul, G.; Ros, R.; Michelin, R. A. *Inorg. Chem.* **1982**, *21*, 495.

(19) Strukul, G.; Michelin, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1538. Italian Patent, Application 23695 A/83 to Consiglio Nazionale delle Ricerche.

[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Table I. pH Measurements of Pt–OH Complexes in MeOH/H₂O Mixture (9/1 Vol)

complex	[Pt], M × 10 ⁻⁴	pH	A ^a
(diphoe)Pt(CF ₃)(OH)	11.9	7.6	7.6
	7.8	7.4	
	5.9	7.3	
(diphos)Pt(CF ₃)(OH)	11.0	9.5	9.4
	7.3	9.2	
	5.5	8.8	
(diphoe)Pt(CH ₃)(OH)	9.1	11.2	11.3
	6.1	10.9	
	4.6	10.7	
<i>trans</i> -(PPh ₃) ₂ Pt(CF ₃)(OH)	7.9	8.1	8.4
	5.4	7.6	
	4.1	7.2	
<i>trans</i> -(PPh ₂ Me) ₂ Pt(CF ₃)(OH)	8.8	8.5	8.6
	5.8	8.2	
	4.4	7.8	
<i>trans</i> -(PPh ₃) ₂ Pt(Ph)(OH)	9.5	10.6	10.7
	6.3	10.3	
	4.7	9.7	

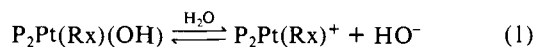
^apH extrapolated graphically at [Pt] = 10⁻³ M from pH vs. -log [Pt] plots.

the premise of a bifunctional role for platinum (base and olefin activator) in this catalytic reaction. With the aim of clarifying the precise requirements concerning the nature of the metal center and the mechanistic details, we now wish to report a more complete description of this system in the epoxidation of 1-octene.

Results and Discussion

Basic Behavior of Pt–OH Complexes. Several indirect evidences can be found in the literature concerning the basic behavior of P₂Pt(Rx)(OH) complexes in solution, including the above-cited reactions with weak acids and the homogeneously catalyzed addition of water to nitriles to give carboxamides.^{11,13,20,21} On the other hand, the only direct measurements of HO⁻ dissociation ability by this class of compounds can be found in previous reports by Otsuka and co-workers²² and by Arnold and Bennett¹³ on compounds of the type *trans*-P₂Pt(Rx)(OH) (P = monophosphine; Rx = H, CH₃, and Ph) which have been found to behave as strong bases in protic media. These authors have suggested^{10,13} that the dissociation ability of these compounds results largely from the electron-donating power of the *trans* anionic ligand Rx (*trans* influence). Measurements of this kind for complexes having a *cis* geometry are completely lacking in the literature. Therefore, we have determined the pH values for some representative complexes among those tested in the epoxidation of 1-octene (*vide infra*). These are reported in Table I. Measurements were carried out in MeOH/H₂O = 9/1 (vol) using different concentrations. A parameter which can be used to compare the basicities of the various complexes is *A* (Table I), that is, the pH extrapolated at 10⁻³ M from pH vs. -log [Pt] plots. As it appears from Table I, a correlation between the complex geometry and basicity cannot be easily assessed, the latter reflecting simply the electron-donating (withdrawing) character of the Rx ligand.

Indeed for many of these compounds, spectroscopic parameters indicate a considerable covalent character for the Pt–O bond under anhydrous conditions,¹⁴ thereby suggesting the important solvolytic role of water in promoting ionic dissociation (reaction 1). This



behavior was confirmed by molar conductivity data taken either in anhydrous or in water-mixed solvents. The results are reported in Table II, where the data relative to two 1/1 electrolytes closely related to this class of hydroxo complexes are also included for comparison. In all cases, addition of 10% H₂O to the solvent produced an increase in the molar conductivity.

Table II. Molar Conductivity (Ω⁻¹ mol⁻¹ cm²) of Pt–OH and Related Complexes in Various Solvent Mixtures (10⁻³ M Solutions)

complex	THF	THF/H ₂ O ^a	MeOH	MeOH/H ₂ O ^a
(diphoe)Pt(CF ₃)(OH)	0.7	1.5	5.3	5.8
(diphoe)Pt(CF ₃)(OOH)	0.4	0.9	4.3	5.2
(diphos)Pt(CF ₃)(OH)	0.1	0.5	3.5	4.8
(diphoe)Pt(Ph)(OH)	1.9	2.1	10.3	10.7
(diphoe)Pt(CH ₃)(OH)	6.1	11.5	23.5	22.0
[(diphoe)Pt(CF ₃)(CH ₂ Cl ₂)]-BF ₄	10.0	35.0	78.0	64.0
<i>trans</i> -(PBz ₃) ₂ Pt(Ph)(OH)	0.5	2.7	11.1	15.6
<i>trans</i> -(PCy ₃) ₂ Pt(CH ₃)(OH)	0.1	1.5	6.7 ^b	
<i>trans</i> -(PPh ₃) ₂ Pt(CF ₃)(OH)	0.2	0.8	3.9	4.5
<i>trans</i> -(PPh ₂ Me) ₂ Pt(CF ₃)(OH)	0.3	0.7	5.0	7.1
[(PPh ₃) ₂ Pt(CF ₃)(CH ₂ Cl ₂)]-BF ₄	5.7	35.0	75.0	61.0

^a10% H₂O. ^bSaturated ~5 × 10⁻⁴ M.

Table III. ³¹P{¹H} NMR Behavior of (A) and (B)

solvent	%H ₂ O added	δ (P ₁) ^a	δ (P ₂) ^b	² J _{P-P}	¹ J _{P₁-Pt}	¹ J _{P₂-Pt}
A						
CD ₂ Cl ₂	0	36.77	48.62	13.8	3451	1792
Me ₂ SO- <i>d</i> ₆	0	36.29	45.45	15.7	3348	1816
	5	36.21	46.60	15.6	3427	1809
	15	36.10	47.37	15.5	3484	1803
	THF ^c	0	36.56	43.97	13.5	3317
THF ^c	5	36.84	47.38	13.8	3480	1798
	10	36.97	49.22	14.1	3566	1789
	15	36.94	49.61	14.6	3587	1791
	20	36.94	49.94	14.5	3605	1790
	25	36.93	50.08	14.1	3612	1790
B						
THF ^c	0	33.84	55.31	15.9	4260	1751
THF ^c	10	33.99	55.36	15.9	4248	1734
	20	33.98	55.36	15.9	4242	1734

^aδ in ppm. ^bJ in Hz. ^cD₂O external lock.

In order to get a more precise figure of the effect of water on the nature of the Pt–OH bond and hence on reaction 1, we also carried out an NMR investigation of the P–Pt coupling constants of (diphoe)Pt(Ph)(OH). The ³¹P{¹H} NMR spectrum of this complex shows as expected two doublets, arising from independent phosphorus nuclei, each with Pt satellites. As suggested by Appleton and Bennett²³ for a series of (diphos)Pt(CH₃)X complexes (X = anionic ligand), the extent of the ¹J_{P-Pt} for the phosphorus *trans* to X is diagnostic of the *trans* influence of the ligand X or, in other words, the more or less pronounced ionic character of the Pt–X bond. Typical extremes are X = CH₃ and X = ONO₂ for which ¹J_{P-Pt} = 1794 and 4510 Hz have been observed, respectively.²³ The OH ligand falls at about half-way (3546 Hz), indicating a considerable covalent character for the Pt–O bond.²³ This behavior has been further confirmed by us for other hydroxo, hydroperoxo, and *tert*-butyl peroxy complexes of platinum(II) where ¹J_{P-Pt} ranges from ~3100 to ~3500 Hz.¹⁴ (diphoe)Pt(Ph)(OH) is no exception; however, addition of H₂O to the initially anhydrous solvent produces some significant variations (Table III) in both the ¹J_{P-Pt} for the phosphorus *trans* to OH and the chemical shift for the phosphorus *cis* to OH. In THF solvent, the former increases ~300 Hz with 0–25% H₂O added, while the latter moves ~6 ppm downfield. This behavior, which accounts for a significant increase in the ionic character of the Pt–O bond, may

(20) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 3030.

(21) Ros, R.; Renaud, J.; Roulet, R. *J. Organomet. Chem.* **1976**, *104*, 271.

(22) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027.

(23) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738.

Table IV. Epoxidation of 1-Octene with Hydrogen Peroxide Catalyzed by Platinum(II) Complexes

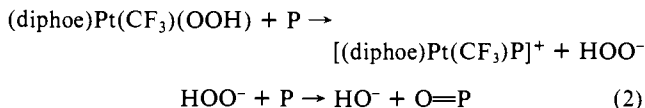
entry	catalyst	initial rate M s ⁻¹ × 10 ⁻⁶	solvent	H ₂ O ₂ , % ^a
1	(diphoe)Pt(CF ₃)(OH)	1.8	THF	35
2	(diphoe)Pt(CF ₃)(OH)	4.9	EtOH	35
3	(diphoe)Pt(CF ₃)(OOH)	0.34	THF	35
4	(diphos)Pt(CF ₃)(OH)	0.21	THF	35
5	(diphos)Pt(CF ₃)(OH)	1.3	EtOH	35
6	(diphoe)Pt(CH ₃)(OH)	=	THF, CH ₂ Cl ₂ /H ₂ O	35
7	(diphoe)Pt(Ph)(OH)	1.0	THF	35
8	(diphoe)Pt(Ph)(OH)	0.05	EtOH	35
9	<i>trans</i> -(PPh ₃) ₂ Pt(CF ₃)(OH)	=	THF	35
10	<i>trans</i> -(PPh ₂ Me) ₂ Pt(CF ₃)(OH)	=	EtOH	35
11	<i>trans</i> -(PCy ₃) ₂ Pt(CH ₃)(OH)	=	THF, EtOH	35
12	<i>trans</i> -(PPh ₃) ₂ Pt(Ph)(OH)	=	THF, EtOH	35
13	<i>trans</i> -(PBz ₃) ₂ Pt(Ph)(OH)	=	EtOH	35
14	<i>cis</i> -(PPh ₃) ₂ Pt(Bz)(OH)	=	THF, EtOH	35
15	(diphoe)Pt(CF ₃)(OH)	11	CH ₂ Cl ₂ /H ₂ O	35
16	[(diphoe)Pt(CF ₃)(CH ₂ Cl ₂)]BF ₄	17	THF	35
17	[(diphoe)Pt(CF ₃)(CH ₂ Cl ₂)]BF ₄	110	CH ₂ Cl ₂ /H ₂ O	35
18	[(diphoe)Pt(CH ₃)(CH ₂ Cl ₂)]BF ₄	=	THF, CH ₂ Cl ₂ /H ₂ O	35
19	[(diphoe)Pt(CF ₃)(CH ₂ Cl ₂)]BF ₄	108	CH ₂ Cl ₂ /H ₂ O	18
20	[(diphoe)Pt(CF ₃)(CH ₂ Cl ₂)]BF ₄	93	CH ₂ Cl ₂ /H ₂ O	12
21	[(diphoe)Pt(CF ₃)(CH ₂ Cl ₂)]BF ₄	26	CH ₂ Cl ₂ /H ₂ O	5

^aConcentration of the original H₂O₂ solution before introduction into the catalytic system; see Experimental Section. Experimental conditions: [Pt], 1.7 × 10⁻² M; [1-octene], 7.4 × 10⁻¹ M; [H₂O₂], 4.2 × 10⁻¹ M.

again be interpreted in terms of the solvolysis process shown in reaction 1 by assuming that what is actually observed in the NMR spectra is the fast interconversion between the two Pt species (neutral and cationic). Attempts to substantiate this view from variable-temperature NMR experiments were unsuccessful since lowering the temperature from 38 to 25 °C resulted in precipitation of the complex. However it is significant that the cationic complex [(diphoe)Pt(Ph)(H₂O)]BF₄, prepared from (diphoe)Pt(Ph)(OH) and HBF₄ according to the method outlined by Appleton and Bennett,²³ shows the ³¹P{¹H} NMR parameters reported in Table III when dissolved in THF.

The extent of the equilibrium depicted in reaction 1 can be influenced also by the presence of molecules capable of occupying the coordination site left vacant by the leaving HO⁻. In the presence of good donor ligands (for example, a phosphine), equilibrium 1 can be completely shifted to the right even under anhydrous conditions as is demonstrated by the experiment described in Figure 1. Increasing amounts of free phosphine were added to a 10⁻³ M solution in DCE (1,2-dichloroethane) of (diphoe)Pt(CF₃)(OH) (a relatively modest base according to Table I), and the corresponding conductivities were monitored. As shown, the initial molar conductivity is negligible; however, upon addition of free phosphine, it increases rapidly, and in the case of P(*n*-Bu)₃, a 4/1 molar excess produces values corresponding to complete dissociation.²⁴

Since the behavior described in Figure 1 for hydroxo complexes will reasonably apply to the corresponding hydroperoxo complexes, this "basic" dissociation is thought to be the key feature in the already described oxidation of free phosphines by P₂Pt(Rx)(OOH) complexes.¹⁸ In fact, the reactivity of these complexes toward P(*n*-Bu)₃ and PPh₃ parallels the trend shown in Figure 1; i.e., the reaction rate for the oxidation of P(*n*-Bu)₃ ≫ PPh₃.²⁵ We infer that the oxidation of phosphines will result from interaction of the free added ligand with the hydroperoxide anion out of the coordination sphere of the metal (reaction 2). This view explains



why it is only the added phosphine to be oxidized and is in agreement with the mechanism proposed by Halpern for the oxidation of phosphines with P₂PtO₂ complexes.²⁶

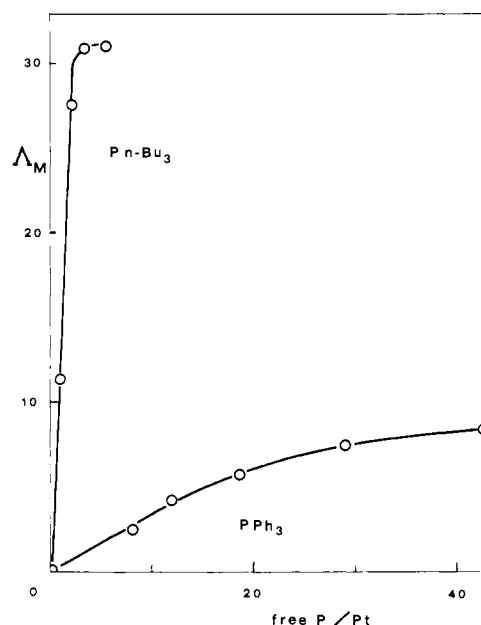


Figure 1. Effect of the addition of free phosphine on the molar conductivity of (diphoe)Pt(CF₃)(OH) in DCE solution (10⁻³ M).

Epoxidation of 1-Octene. When 35% H₂O₂ is added to a THF solution of (diphoe)Pt(CF₃)(OH) containing an excess of 1-octene, selective epoxidation of the olefin takes place. The reaction profile at 20 °C (Figure 2D) shows a linear initial rate until ~30–40% conversion and then proceeding to the complete consumption of H₂O₂ to yield only the epoxide, thus indicating the absence of side reactions. Typically under these experimental conditions, terminal olefins are oxidized while internal olefins are not.¹⁹ Selectivity is in all cases >99% since epoxides are the only detectable oxidation products.

We have tested in this reaction a series of P₂Pt(Rx)(OH) complexes under experimental conditions similar to those reported above. In most cases, plots of epoxide formed vs. time display the typical features depicted in Figure 2D. The initial rates for the epoxidation of 1-octene are reported in Table IV. The first observation that appears evident is that monophosphine derivatives are not active catalysts (Table IV, entries 9–14). This fact is associated with the experimental observation that the initially

(24) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(25) Strukul, G. et al., unpublished results.

(26) Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8337.

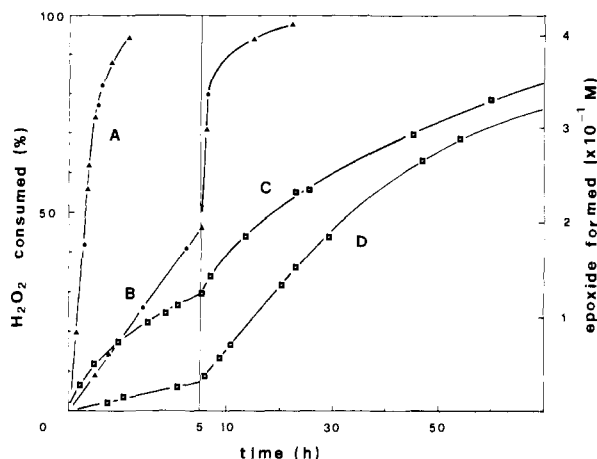
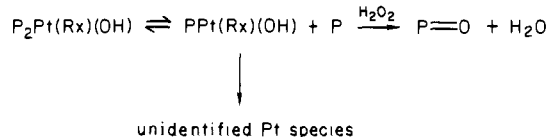


Figure 2. Reaction profiles for the epoxidation of 1-octene with 35% H_2O_2 catalyzed by Pt(II) complexes. (A) $[(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{CH}_2\text{Cl}_2)]\text{-BF}_4$ in $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$; (B) $(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{OH})$ in $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$; (C) $[(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{CH}_2\text{Cl}_2)]\text{BF}_4$ in THF; (D) $(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{OH})$ in THF. Experimental conditions as in Table IV.

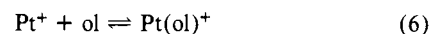
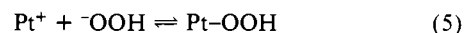
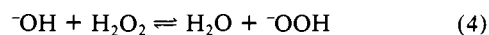
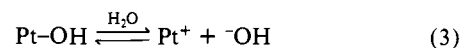
colorless reaction mixtures turned more or less rapidly yellow (10–200 min).

Most of the compounds reported in Table IV are known to form stable hydroperoxo complexes by reaction with 35% H_2O_2 .^{14,17,18} The reactivity shown in the epoxidation of 1-octene parallels the ease with which the hydroperoxo complexes can be prepared, i.e., $(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{OOH}) \sim (\text{diphos})\text{Pt}(\text{CF}_3)(\text{OOH}) > \text{trans-}(\text{PPh}_2\text{Me})_2\text{Pt}(\text{CF}_3)(\text{OOH}) \gg \text{trans-}(\text{PPh}_3)_2\text{Pt}(\text{CF}_3)(\text{OOH}) \sim \text{trans-}(\text{PPh}_3)_2\text{Pt}(\text{Ph})(\text{OOH}) \sim (\text{diphoe})\text{Pt}(\text{CH}_3)(\text{OOH})$. Hydroperoxo species of $\text{trans-}(\text{PCy}_3)_2\text{Pt}(\text{CH}_3)(\text{OH})$, $\text{trans-}(\text{PBz}_3)_2\text{Pt}(\text{Ph})(\text{OH})$, and $\text{cis-}(\text{PPh}_3)_2\text{Pt}(\text{Bz})(\text{OH})$ have not been isolated. During the preparation of monophosphine-PtOOH derivatives, the occurrence of yellow-orange solutions is a frequently encountered problem which results in lower yields. In order to have a better understanding of the nature of this undesired reaction, we carried out the following experiment: $\text{trans-}(\text{PPh}_3)_2\text{Pt}(\text{Ph})(\text{OH})$ was dissolved in EtOD, and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was recorded (δ 23.44 (s, $^1J_{\text{P-Pt}} = 3290$ Hz)). Then 35% H_2O_2 was added in a $\sim 10/1$ molar excess with respect to Pt. After ~ 3 h, a new spectrum was run. The signals corresponding to the starting complex were reduced to $\sim 1/2$ and new signals were present: a sharp singlet at 30.94 ppm typical of $\text{Ph}_3\text{P}=\text{O}$ and a complicated multiplet centered at ~ 22 ppm with evidence for P–Pt couplings. We tested under similar experimental conditions $(\text{diphoe})\text{Pt}(\text{Ph})(\text{OH})$ which, conversely, showed no evidence for phosphine oxide formation. These results suggest that monophosphine complexes undergo phosphine ligand dissociation which, in the presence of free H_2O_2 , is very rapidly oxidized.



PtOOH species once isolated are relatively stable both in the solid state and in solution. Although clearly involved in the above described catalytic process, they do not appear to be the active species, as demonstrated by the observation that they do not transfer oxygen to olefins in anhydrous media even under forcing conditions.^{17,18} However, when an excess of H_2O_2 is added to a solution of 1-octene in the presence of catalytic amounts of $(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{OOH})$, epoxydation of the olefin takes place with features similar to those reported in Figure 2D. This effect is ascribed to solvolysis by water according to reaction 1 as the critical step.

Mechanism. If we try to provide a mechanistic basis for the epoxidation process, the chemistry so far reported suggests for the active platinum complexes the following set of equilibria (ol = olefin):



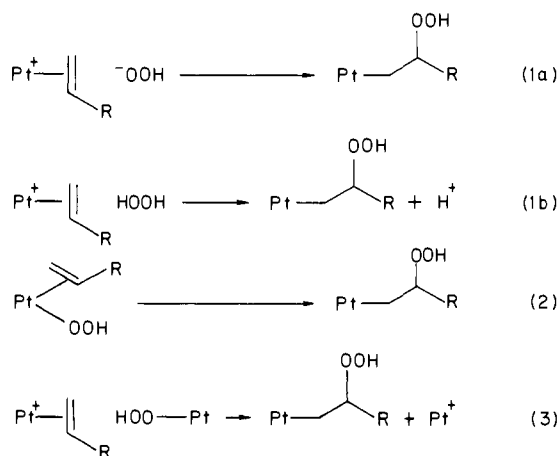
External attack from a nucleophile onto the coordinated olefin seems the most likely step for the formation of the epoxide (vide infra) as is also suggested by the reactivity pattern toward different olefins.¹⁹ The above-reported parallelism between the stability of the PtOOH complexes and the initial rate data of Table IV indicates that the extent of the equilibria 3–5 is very important to the efficiency of the system. On the other hand, since in many cases the extent of the equilibrium 3 is relatively modest, the concentration of the unsaturated Pt^+ species in the catalytic system is likely to be rather low. If this is so, the use as catalysts of cationic complexes of the type $[\text{P}_2\text{Pt}(\text{Rx})]^+$ might lead to a significant increase in the initial rate. We tested under the usual experimental conditions the complex $[(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{CH}_2\text{Cl}_2)]\text{BF}_4$. The reaction profile is reported in Figure 2C. As shown, the initial high concentration of cationic olefin complex results in an estimated increase in the initial rate of about an order of magnitude (Table IV, entry 16). However, after the initial jump (Figure 2C), the system rapidly deactivates and approximates the behavior observed for neutral complexes. At the end of the catalysis, when H_2O_2 was completely consumed, the reaction mixture was concentrated to small volume and the metallic species were isolated by addition of Et_2O . IR analysis (Nujol) of the solid showed evidences for coordinated H_2O (3670 cm^{-1}) and BF_4^- (1050 – 1060 cm^{-1}) plus a medium-weak band at 3580 cm^{-1} typical of the coordinated OH ligand which might well be attributed to $(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{OH})$ (3625 cm^{-1} in the pure state).¹⁷ The data here reported support the above reaction sequence and demonstrate that under the experimental conditions used in the catalysis, PtOH species can form also from Pt^+ and $\text{H}_2\text{O}/\text{H}_2\text{O}_2$.

In this catalytic system, the achievement of high reaction rates is limited by the modest efficiency with which the metal center interacts with the olefin. The use of THF or other water-miscible solvents¹⁹ constitutes a severe limitation since the solvent and $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ may compete favorably with the olefin to bind on the vacant coordination site of the $[\text{P}_2\text{Pt}(\text{Rx})]^+$ species. From this point of view, the use of a biphasic reaction medium should be potentially very useful, since water-immiscible solvents are generally very weak donor ligands. When an excess of 35% H_2O_2 was added to a solution of either $[(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{CH}_2\text{Cl}_2)]\text{BF}_4$ or $(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{OH})$ in CH_2Cl_2 containing an excess of 1-octene, the reaction profiles shown in Figure 2A and 2B were observed, respectively. As shown, the initial rates are greatly increased (1.1×10^{-4} and 1.1×10^{-5} M s^{-1} , respectively) with respect to the corresponding monophasic systems; moreover the plots are linear until $\sim 80\%$ conversion, which represents a significant advantage for practical purposes. Further dilution of the H_2O_2 solution (Table IV, entries 17 and 19–21) appears to become a limiting factor below 18% although considerable efficiency is maintained even at 5% concentration (initial rate 2.6×10^{-5} M s^{-1}).

Indeed the $-\text{CF}_3$ derivatives are by far the most stable and reactive catalysts for this epoxidation reaction when compared to $-\text{Ph}$ or $-\text{CH}_3$ derivatives (Table IV, entries 1, 2, 6–8, and 18). In fact, the solutions of the latter complexes when in contact with H_2O_2 turn yellow ($(\text{diphoe})\text{Pt}(\text{Ph})(\text{OH}) \sim 24$ h; $(\text{diphoe})\text{Pt}(\text{CH}_3)(\text{OH})$, a few minutes). This behavior may reflect the ease with which the Pt–C bond is hydrolyzed because of the slight acidity of H_2O_2 . In this respect, the Pt–C bond in fluoroalkyl complexes is known to be very stable toward hydrolysis.²⁷ Indeed, when 35% H_2O_2 was added to a THF solution of $(\text{diphoe})\text{Pt}(\text{CH}_3)(\text{OH})$ kept under N_2 at room temperature, the initially

(27) Hartley, F. R. "The Chemistry of Platinum and Palladium"; Applied Science: London, 1973; p 316.

Scheme I



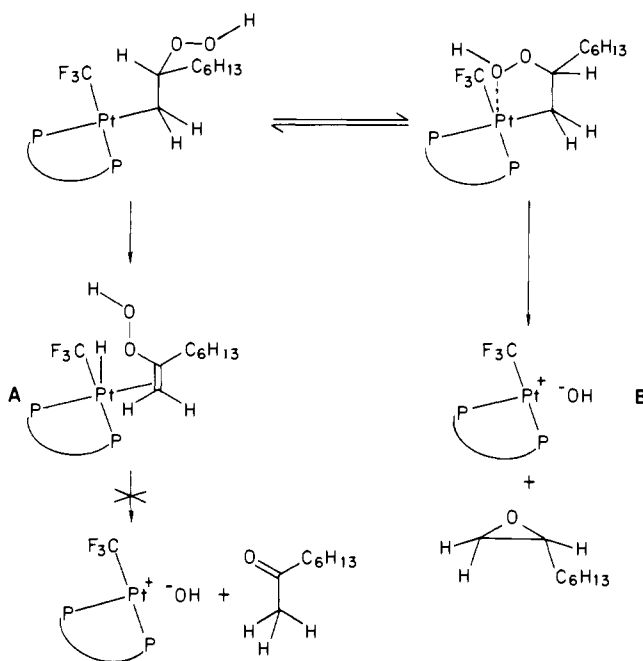
colorless solution turned yellow after ~ 15 min. A sample of the gas phase analyzed with GLC revealed a slow evolution of methane which was quantitative after ~ 2 days. This experiment does prove that H_2O_2 is able to hydrolyze the Pt-C bond of the complex; however, its relevance in the catalytic system is doubtful since, in this case, other pathways (vide infra) leading to the decomposition of the complex may be suggested.

Oxygen-Transfer Step. A discussion of the possible molecular pathways leading to oxygen transfer and epoxide formation in the present system will have to take into account several aspects that make this system rather unusual if compared to previously reported oxidations with groups 8-10 MOOH species,^{28,29} namely, (i) the basic nature of the medium where the reaction takes place, (ii) the involvement of cationic metal-olefin complexes with subsequent nucleophilic attack by the oxidant, (iii) the unusual nature of the oxidation product, and (iv) the absence of any other side product.

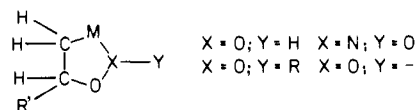
In principle, several possible pathways can be envisaged (Scheme I): (1) external attack by a hydroperoxide anion (a) or a hydrogen peroxide molecule (b); (2) internal insertion of the olefin into the Pt-O bond of a coordinated-OOH ligand; and (3) bimolecular coupling involving two different Pt species. Of these, path 2, which would require in the present case the formation of a five-coordinate intermediate, can be ruled out on the basis of the water-free experiments. However, it has to be pointed out that, to date, type 2 oxygen transfer has been the only one that has been suggested to be involved in alkene oxidations mediated by groups 8-10 transition-metal peroxo species. The other possibilities, which can be regarded as external attacks of a nucleophile onto a coordinated olefinic moiety, have been previously suggested as possible candidates only by Andrews et al. in the air oxidation of olefins catalyzed by Pd- NO_2 complexes.³⁰ Owing to the wide variety of conditions in which the present system has been tested (monophasic or biphasic reaction medium, with Pt^+ or PtOH species as catalysts), it seems unlikely that a single type of nucleophile is operative in all cases, although a choice will be possible only on the basis of kinetic experiments under different conditions which are currently under way.

A metal-alkyl hydroperoxide is produced independently of the nature of the nucleophile which eliminates the epoxide and restores the original metal-hydroxo ion pair. The metal-alkyl hydroperoxide can exist (Scheme II) in two different configurations: open chain and cyclic (quasi-peroxometalacycle). It has to be pointed out that despite widespread suggestions of their involvement in transition-metal-mediated alkene oxidations,⁶

Scheme II



well-characterized examples of metallocycles of the general type indicated below are relatively few.³¹⁻³⁵



In any case, the expected oxidation product from simple oxygen atom transfer to an olefin should, in principle, be the epoxide (Scheme II, route B). Evolution of the metallocycle to the ketone requires hydrogen shift from the β to the α position. This process which is metal-assisted (Scheme II, route A) has been suggested to proceed via metal hydride formation^{36,37} and appears to be favored by coordinative unsaturation of the metal and M-C-C-H dihedral angle = 0° .^{38,39} These two requirements have been circumvented with metal-nitro compounds in at least two cases by using different strategies; Andrews and co-workers have employed sterically rigid cyclic olefins^{30,35} while Mares and co-workers have used olefin activators such as Tl(III) which are not capable of promoting β -hydride elimination.³⁷ In both of these cases, epoxidation has been obtained.

Therefore, it appears that the factors capable of affecting the position of the starting equilibrium in Scheme II are very important for the nature of the oxidation product. In the present case, route A is not viable since *cis*-hydridoalkyl derivatives of Pt(II), even if formed, do not undergo olefin insertion under mild conditions as has been shown in the case of $\text{P}_2\text{Pt}(\text{R}_x)\text{H}$ complexes (P_2 = diphos, diphoe; R_x = $(\text{CH}_2)_{1-3}\text{CN}$, CF_3).⁴⁰ Route A provides also a reliable explanation for the decomposition of -Ph or - CH_3 derivatives, since, in this case, the hydridoolefin intermediate is

(28) Roussel, M.; Mimoun, H. *J. Org. Chem.* **1980**, *45*, 5381. Igersheim, F.; Mimoun, H. *Nouv. J. Chim.* **1980**, *4*, 711.

(29) Atlay, M. T.; Preece, M.; Strukul, G.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1982**, 406. Atlay, M. T.; Preece, M.; Strukul, G.; James, B. R. *Can. J. Chem.* **1983**, *61*, 1332.

(30) Andrews, M. A.; Chang, T. C. T.; Cheng, C. W. F.; Kelly, K. P. *Organometallics* **1984**, *3*, 1777.

(31) Sheldon, R. A.; Van Doorn, J. A. *J. Organomet. Chem.* **1975**, *94*, 115.

(32) Halfpenny, J.; Small, R. W. H. *J. Chem. Soc., Chem. Commun.* **1979**, 879.

(33) Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5832.

(34) Broadhurst, M. J.; Brown, J. M.; John, M. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 47.

(35) Andrews, M. A.; Chang, T. C. T.; Cheng, C. W. F.; Kelly, K. R.; Koetzle, T. F. *J. Am. Chem. Soc.* **1984**, *106*, 5913.

(36) Andrews, M. A.; Cheng, C. W. F. *J. Am. Chem. Soc.* **1982**, *104*, 4268.

(37) Diamond, S. E.; Mares, F.; Szalkiewicz, A.; Muccigrosso, D. A.; Solar, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 4266.

(38) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.

(39) Reger, D. L.; Culbertson, E. C. *J. Am. Chem. Soc.* **1976**, *98*, 2789.

(40) Ros, R.; Michelin, R. A.; Bataillard, R.; Roulet, R. *J. Organomet. Chem.* **1979**, *165*, 107. Michelin, R. A.; Ros, R., unpublished results.

also a *cis*-hydridoalkyl (aryl) species which are known to rapidly undergo reductive elimination,⁴¹ at variance with (diphoe)Pt-(CF₃)H that has been found to be very stable.⁴⁰

The metal-alkyl hydroperoxide intermediate can be regarded as a true quasi-peroxymetallocycle rather than an open-chain species, since molecular models indicate the possibility of an easy interaction between the metal and the second oxygen from the axial position. Under these circumstances, removal of the relatively stable Pt...OH interaction followed by opening of the cycle and interaction with the less close β -hydrogen to produce a five-coordinate hydridoolefin intermediate may be a rather unfavorable process. This view is supported also by the previously reported stoichiometric epoxidation of cyclic olefins with perbenzoato complexes of Pt(II)⁴² and accounts also for the observed selective ketonization of terminal olefins at 80 °C by the closely related *trans*-P₂Pt(Rx)(OO-*t*-Bu) complexes.¹⁴ In fact, in this case, the very bulky *t*-Bu group cannot be easily accommodated between the mutually *trans*-phosphine ligands, thereby favoring the open-chain configuration. As exemplified by the present platinum-based systems, we believe that the relative stability of the cyclic vs. open-chain metal-alkyl hydroperoxide intermediates (i.e., the starting equilibrium of Scheme II) could be regarded as a useful argument to predict the nature of the oxidation products.

Conclusion

The catalytic system described in this paper seems to represent a breakthrough in the use of inexpensive, nonpolluting solutions of H₂O₂ as the epoxidizing agent for simple, terminal olefins. Moreover, since it does not suffer from the limitations exposed in the Introduction, it appears potentially attractive for practical applications.

We believe that the crucial clue to the success of this oxygenating system lies mainly in the high stability of the bonding interactions from the chelating diphosphine and fluoroalkyl ligands, which allow the platinum(II) hydroxo complexes to behave as bifunctional reagents. In fact, from the one hand, they can exploit their basic behavior to enhance H₂O₂ reactivity through the formation of the hydroperoxide anion and PtOOH species and, on the other hand, they activate otherwise unreactive terminal olefins toward nucleophilic attack. However, while the viability of the system appears to be in good agreement with the strategy devised in the Introduction and hence on electronic factors, the high selectivity in the epoxide formation seems to respond rather to geometric implications, i.e., the possibility of forming and stabilizing the intermediate quasi-peroxymetallocycle.

Experimental Section

Apparatus. IR spectra in Nujol mulls were taken on a Perkin-Elmer 597 spectrophotometer using CsI plates. ¹H and ³¹P{¹H} NMR spectra were recorded on a Varian FT 80A spectrometer operating in FT mode, using as references internal Me₄Si or external H₃PO₄, respectively. Negative chemical shifts are upfield from the reference. GLC measurements were taken on a Perkin-Elmer 3920 gas chromatograph equipped with a Hewlett-Packard 3370B electronic integrator. Identification of products was made with GLC by comparison with authentic samples. Conductivity measurements were made with a AMEL 123 instrument using 10⁻³ M solutions unless otherwise stated. pH measurements in a MeOH/H₂O (9/1 vol) mixture were determined on a ORION 701 digital pH meter.

Materials. Solvents were dried and purified according to standard methods. 1-Octene (Fluka) was purified by passing through neutral alumina, distilled, and stored under N₂ in the dark. Hydrogen peroxide (35%) (Fluka) was a commercial product and used without purification.

The preparation of the complexes used in the catalytic reactions was performed under dry N₂ by conventional Schlenk and syringe techniques.

The following compounds were prepared by literature methods: (diphoe)Pt(CF₃)(OH),¹² (diphos)Pt(CF₃)(OH),¹² *trans*-(PPh₃)₂Pt(CF₃)(OH),¹² *trans*-(PPh₂Me)₂Pt(CF₃)(OH),¹² [(diphoe)Pt(CF₃)(CH₂Cl₂)]-BF₄,¹² [(PPh₃)₂Pt(CF₃)(CH₂Cl₂)]BF₄,¹² (diphoe)Pt(CF₃)(OOH),¹⁸ (diphoe)Pt(CH₃)(OH),²³ [(diphoe)Pt(CH₃)(acetone)]BF₄,²³ *trans*-

(PPh₃)₂Pt(Ph)(OH),¹⁰ *trans*-(PBz₃)₂Pt(Ph)(OH),¹⁴ (COD)Pt(CH₃)Cl,⁴³ (COD)Pt(Ph)Cl,⁴³ 1,2-epoxyoctane.⁴⁴

New Complexes. A few new complexes were prepared. They are air-stable in the solid state, and they all give satisfactory elemental analyses (C, H) for the proposed structures.

(diphoe)Pt(Ph)Cl. (COD)Pt(Ph)Cl (1.05 g, 2.53 mmol) was dissolved in N₂-saturated CH₂Cl₂ (30 mL). To the stirred solution, kept under N₂, diphoe (1.00 g, 2.53 mmol) was added as solid. After a few minutes, a white solid started precipitating. The mixture was stirred overnight and concentrated in vacuo. Et₂O was added to complete precipitation. The solid was filtered, washed with Et₂O, and dried: recrystallized CH₂Cl₂/Et₂O. (yield 98%); IR (cm⁻¹) 301 (m, $\nu_{\text{Pt-Cl}}$); ³¹P{¹H} NMR (CD₂Cl₂) δ 40.06 (d, *trans*-Cl, ²J_{P-P} = 9.9, ¹J_{P-Pt} = 4210 Hz), 51.92 (d, *trans*-Ph, ²J_{P-P} = 9.9, ¹J_{P-Pt} = 1685 Hz).

(diphoe)Pt(Ph)(OH). (diphoe)Pt(Ph)Cl (1.67 g, 2.38 mmol) was suspended in N₂-saturated acetone (30 mL). A solution of AgBF₄ (0.47 g, 2.4 mmol) in acetone (20 mL) was added under N₂. The mixture was stirred overnight. AgCl was filtered off, and the filtrate was concentrated to about one-half in vacuo. KOH (0.14 g, 2.4 mmol) dissolved in H₂O (8 mL) was added dropwise. The mixture was stirred for 0.5 h and then concentrated slowly to dryness in vacuo. The solid residue was extracted with three 10-mL portions of a 1/1 toluene/CH₂Cl₂ mixture. The solution was concentrated in vacuo to 8–10 mL and then placed to -20 °C for 2 h. A white solid separated which was filtered, washed with Et₂O, and dried: recrystallized toluene/Et₂O (yield 60%); IR (cm⁻¹) 3600 (w, $\nu_{\text{O-H}}$), 512 (m, $\nu_{\text{Pt-O}}$); ³¹P{¹H} NMR see Table III.

[(diphoe)Pt(Ph)(H₂O)]BF₄. (diphoe)Pt(Ph)(OH) (0.16 g, 0.23 mmol) was dissolved in CH₂Cl₂ (5 mL). A solution of HBF₄ (0.46 mL) (0.5 M in H₂O) was added dropwise. The mixture was stirred at room temperature for 10 min and then brought to dryness. The residue was dissolved in CH₂Cl₂ (5 mL) and treated with a few drops of H₂O. *n*-Hexane was added (20 mL) to give a cream product, which was filtered and air-dried: (yield 73%); IR (cm⁻¹) 3550 (w, $\nu_{\text{O-H}}$), 1620 (w, $\delta_{\text{O-H}}$); ³¹P{¹H} NMR see Table III.

***trans*-(PCy₃)₂Pt(CH₃)Cl.** This was prepared as (diphoe)Pt(Ph)Cl from (COD)Pt(CH₃)Cl (1.94 g, 5.5 mmol) and PCy₃ (3.08 g, 11.0 mmol): yield 95%; IR (cm⁻¹) 275 (m, $\nu_{\text{Pt-Cl}}$); ¹H NMR (CD₂Cl₂) δ 0.29 (t, CH₃, ³J_{H-P} = 5.3, ²J_{H-Pt} = 82.2 Hz); ³¹P{¹H} NMR (CD₂Cl₂) δ 21.00 (s, ¹J_{P-Pt} = 2823 Hz).

***trans*-(PCy₃)₂Pt(CH₃)(OH).** *trans*-(PCy₃)₂Pt(CH₃)Cl (4.21 g, 5.23 mmol) and AgClO₄ (1.08 g, 5.23 mmol) were placed solid in a Schlenk flask under N₂. N₂-saturated CH₂Cl₂ (50 mL) was added, and the mixture was stirred overnight at room temperature. AgCl was filtered off, and the filtrate was brought to dryness in vacuo. The solid residue was dissolved in about 150 mL of acetone, and to the solution was added KOH (0.32 g, 5.7 mmol) dissolved in 10 mL of H₂O dropwise with stirring. The mixture was stirred for 5 h, during which slow precipitation of a white solid occurred. Concentration to complete dryness yielded a white residue which was extracted several times with toluene. The toluene solution was concentrated to small volume, and hexane was added to give a white precipitate. This was filtered, washed with small portions of hexane, and dried: recrystallized toluene/hexane (yield 55%); IR (cm⁻¹) 3625 (w, $\nu_{\text{O-H}}$); ¹H NMR (CD₂Cl₂) δ -0.03 (t, CH₃, ³J_{H-P} = 4.9, ²J_{H-Pt} = 74.6 Hz); ³¹P{¹H} NMR (CD₂Cl₂) δ 23.56 (s, ¹J_{P-Pt} = 2904 Hz).

Catalytic Reactions. These were carried out in a 25-mL round-bottomed flask equipped with a stopcock for vacuum/N₂ operations and a side arm fitted with a screw-capped silicone septum to allow sampling. Constant temperature (20 °C) was maintained by water circulation through an external jacket connected with a thermostat. Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer. Either water-miscible solvents (THF and EtOH) or a two-phase system (CH₂Cl₂/H₂O) were employed.

The general procedure here reported was followed in all cases. In a typical experiment, (diphoe)Pt(CF₃)(OH) (68 mg, 0.10 mmol) was placed in the reactor which was evacuated and placed under N₂ atmosphere. Dry, N₂-saturated THF (5 mL) was added, followed by 1-octene (0.70 mL, 4.4 mmol). After stirring a few minutes, 35% H₂O₂ solution (0.25 mL, 2.5 mmol) was injected, and the time was started. The reaction was monitored with GLC by periodically sampling the reaction mixture with a microsyringe. Separation of the products was performed on a 2-m 10% UCC on Chromosorb W column using a thermal conductivity detector. In experiments employing more diluted H₂O₂ solutions, these were prepared prior to use by adding appropriate amounts of H₂O to 35% H₂O₂.

Acknowledgment. We thank the Consiglio Nazionale delle Ricerche (Rome) for financial support through an operating grant

(41) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915. Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, C17.

(42) Chen, M. J. Y.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1977**, 204.

(43) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

(44) Swern, D. *Org. React.* **1953**, *7*, 378.

of the "Progetto Finalizzato Chimica Fine e Secondaria". Thanks are also expressed to Dr. Fulvio Di Furia (University of Padua) for many helpful discussions and suggestions.

Registry No. (diphoe)Pt(CF₃)(OH), 70504-87-9; (diphoe)Pt(CF₃)(OOH), 72953-62-9; (diphoe)Pt(Ph)(OH), 98839-52-2; *trans*-(PPh₃)₂Pt(CF₃)(OH), 71588-93-7; *trans*-(PPh₂Me)₂Pt(CF₃)(OH), 71588-94-8; *trans*-(PCy₃)₂Pt(CH₃)(OH), 98839-53-3; *trans*-(PBz₃)₂Pt-

(Ph)(OH), 87249-53-4; *cis*-(PPh₃)₂Pt(Bz)(OH), 87249-55-6; [(diphoe)Pt(CF₃)(CH₂Cl₂)]BF₄, 98839-55-5; (diphoe)Pt(Ph)Cl, 98839-56-6; [(diphoe)Pt(Ph)(H₂O)]BF₄, 98839-58-8; *trans*-(PCy₃)Pt(CH₃)Cl, 98839-59-9; *trans*-(PPh₃)₂Pt(Ph)(OH), 60399-83-9; (diphos)Pt(CF₃)(OH), 72953-78-7; (diphoe)Pt(CH₃)(OH), 98839-60-2; [(diphoe)Pt-(CH₃)(CH₂Cl₂)]BF₄, 98839-62-4; [(PPh₃)₂Pt(CF₃)(CH₂Cl₂)]BF₄, 98839-64-6; (COD)Pt(Ph)Cl, 51177-65-2; (COD)Pt(CH₃)Cl, 50978-00-2; 1-octene, 111-66-0; 1-octene epoxide, 2984-50-1.

Theoretical Study of the Tautomeric Equilibrium of 4(1*H*)-Pyridinone in Solution

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Abstract: A semiempirical potential, obtained from accurate ab initio calculations, has been used in the study of the solvation of the tautomeric forms of the 4(1*H*)-pyridinone. Ninety-two water molecules have been included in the calculation. The calculation predicts the lactam tautomer to be the most stable form in aqueous solution. The calculated relative stabilization energy is in satisfactory agreement with the experimental value. The reduced computer time needed in these calculations, as compared with other methods, and the goodness of the results obtained suggest that the present method may be a very useful tool for the study of solvation problems.

The study of solvation is essential to our understanding of the chemical and, particularly, biochemical processes, which take place in (aqueous) solution.

In order to make the theoretical treatment tractable, several approximate models of the interactions in solvated systems have been proposed in recent years.¹ All of these models, however, require large amounts of computer time, which limits their practical applicability. And, consequently, there is still a need for methods, which are not too expensive computationally and are capable, at the same time, of providing adequately accurate results.

The common characteristics of these methods is the use of additive pair potentials for either atom-atom or site-site interactions. These potentials may be derived by parametrization of (energetic and/or structural) experimental data or by fitting of accurate theoretical results.² A formulation, based on the latter approach, has been developed recently at this laboratory.³

In this work we report the results obtained in the application of such a method to a chemical problem in which solvation plays an extremely important role: the tautomeric equilibrium between the lactim and lactam forms of the 4(1*H*)-pyridinone. The method has already been used in studies of solvation-related problems,⁴⁻⁷ and in all cases the agreement with the experimental results was satisfactory.

Theoretical Details

Method. The method used in the calculations was originally proposed for the general study of molecular interaction problems.³

(1) Berndt, M.; Kwiatkowski, J. S. In "Theoretical Chemistry of Biological Processes"; Naray-Szabo, G., Ed.; Elsevier Science Publishers: Amsterdam, in press.

(2) See ref 1 for an exhaustive review of existing intermolecular potentials.

(3) Fraga, S. J. *Comput. Chem.* **1982**, *3*, 329-334. Fraga, S. *Comput. Phys. Commun.* **1983**, *29*, 351-359. This program has been modified in order to carry out an automatized generation of solvation clusters.

(4) Fraga, S. In "Current Aspects of Quantum Chemistry"; Carbo, R. Ed.; Elsevier Science Publishers: Amsterdam, 1982; "Studies in Physical and Theoretical Chemistry", Vol. 21.

(5) Fraga, S. *Can. J. Phys.* **1983**, *61*, 680-682.

(6) Fraga, S. J. *Mol. Struct.-Theochem.* **1983**, *94*, 251-260.

(7) Sordo, J. A.; Klobukowski, M.; Fraga, S. *Can. J. Phys.*, in press.

The interaction energy between two systems, A and B, is evaluated as

$$\Delta E = \sum \sum \Delta E_{ij}$$

where the summations extend over all the possible pairs of atoms, with the restriction that such atoms belong to different molecules. The pair potential ΔE_{ij} takes the form

$$\Delta E_{ij} = 1389.4168q_i q_j / R_{ij} - 694.70838(f_i \alpha_i q_j^2 + f_j \alpha_j q_i^2) / R_{ij}^4 - 1516.0732f_i f_j \alpha_i \alpha_j / [(f_i \alpha_i / n_i)^{1/2} + (f_j \alpha_j / n_j)^{1/2}] R_{ij}^6 + 4.184c_i^{(12)} c_j^{(12)} / R_{ij}^{12}$$

where q_i , α_i , and n_i represent the effective charge, the dipole polarizability, and the effective number of electrons of atom i , respectively. The c_i coefficients and the correction factors f_i were determined on the basis of accurate self-consistent-field (SCF) results and semiempirical considerations.³ R_{ij} stands for the distance between the two interacting atoms. The dispersion contribution to the interaction energy may be optionally included in the calculations.⁸

This method has already been tested in order to determine its ability to represent the interactions in various systems.⁴⁻⁷ Of importance to the present study is the fact that macroscopic properties of bulk water have been predicted extraordinarily well, indicating that the interactions between water molecules are satisfactorily treated in the method. The method has performed equally well in studies on other systems, including solvated amino acids.

It must be emphasized, however, that this is a microscopic, quantum chemical method, in which statistical mechanics is not used. That is, the method yields temperature-independent results which can only be correlated, rather than directly compared, with the experimental values.

Simulation of Solvation Clusters. An existing program,³ implementing the above method, has been appropriately modified in order to generate the solvation cluster in an automatic manner.

The details of the corresponding procedure are as follows. First, the solute is positioned with its center of mass coinciding with the origin of coordinates. Then, a water molecule is placed at a chosen point and left to find, following an energy path of steepest descent, the position at which its interaction energy with the solute is minimum. This calculation is

(8) The data required for the inclusion of the dispersion contribution have been determined by P. Hobza (private communication).