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Kinetic Study of the Epoxidation of 1-Octene with Hydrogen Peroxide Catalyzed by Platinum(II) Complexes. Evidence of the Involvement of Two Metal Species in the Oxygen-Transfer Step

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A detailed kinetic study of the epoxidation of 1-octene with hydrogen peroxide catalyzed by Pt(II) complexes is reported. The two systems analyzed were (diphoe)Pt(CF₃)(OH)/1-octene/H₂O₂/H₂O/THF and [(diphoe)Pt(CF₃)(CH₂Cl₂)]BF₄/1-octene/H₂O₂/H₂O/CH₂Cl₂. Rate data were determined with GLC from epoxide formed vs time plots. Evidence for many of the organometallic intermediates and the individual steps involved was gained from IR studies, ¹⁹F NMR studies, and especially designed experiments including studies of the acidity effect. In both cases the kinetic analysis suggests a mechanism in which the actual oxidant is a PtOOH species that interacts with a Pt-olefin complex in the oxygen-transfer step (second-order dependence on platinum).

Introduction

The discovery of group VIII transition-metal-mediated alkene oxidations with hydroperoxides²⁻⁶ has represented a major breakthrough in this area of chemistry. From a mechanistic point of view these systems have not been adequately characterized, especially as far as the oxygen-transfer step is concerned, although a variety of studies on reactions involving metal-dioxygen complexes with organic electrophiles have appeared over the years.⁷ Compared to the classical d⁰-metal-based systems, they apparently show a number of interesting features that can be summarized as follows, although none of the following points has been directly proved as yet: (i) the function of the metal is 2-fold—it activates otherwise unreactive olefins toward nucleophilic attack and increases hydroperoxide nucleophilicity through coordination; (ii) the roles of the nucleophile and the electrophile are inverted (Scheme I);⁸ (iii) the metal often promotes β-hydride migration with consequent formation of ketones.

From the point of view of possible industrial outputs, the last is often regarded as an undesired event with respect to the more appealing formation of epoxides; however, these systems have allowed the oxidation of unfunctionalized terminal olefins, which are the most difficult to oxidize with the traditional d⁰ systems.¹¹

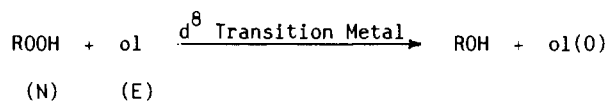
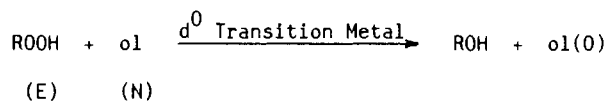
We have recently reported^{5,6} the use of P₂Pt(Rx)X type complexes (P₂ = diphosphines; Rx = CF₃, Ph; X = OH, solvent) as catalysts for the selective (>99%) epoxidation of terminal olefins with diluted H₂O₂ as the primary oxidant, which represents the first reported example of epoxide formation with a group VIII metal/hydroperoxide system. The catalysts have been also modified with chiral diphosphines and allowed to carry out the asymmetric epoxidation of terminal olefins with optical purities up to 41%.¹² The reactivity shown suggests the formation as key reactive intermediate of a metal-olefin complex that is subjected to nucleophilic attack by the oxidant, the nature of which was not determined.⁶ To support the points exposed above, we now wish to report a complete mechanistic description of this system, which provides the first clear evidence of the involvement of two individual metal species in the oxygen-transfer step.

Results

The two systems that were analyzed kinetically are the following: (A) (diphoe)Pt(CF₃)(OH)/1-octene/H₂O₂/H₂O/THF and (B) [(diphoe)Pt(CF₃)(CH₂Cl₂)]BF₄/1-octene/H₂O₂/H₂O/CH₂Cl₂ (diphoe = *cis*-1,2-bis(diphenylphosphino)ethylene). These were chosen because they complement each other and provide cross information, but on the other hand with the employment of different starting platinum complexes some differences in the oxygen-transfer steps were expected.⁶ All kinetic data were obtained from epoxide formed vs time plots derived from GLC measurements.

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Scheme I



N = Nucleophile

E = Electrophile

Table I. Summary of the Kinetic Data Relative to System A^a

10 ³ [Pt] _T , M	[1-octene], M	[H ₂ O ₂], M	[H ₂ O], M	10 ⁷ (rate), M s ⁻¹
2.2	0.74	0.52	2.63	0.8
5.2	0.74	0.52	2.63	4.2
7.4	0.74	0.52	2.63	7.5
14.0	0.74	0.52	2.63	24.0
24.3	0.74	0.52	2.63	52.5
14.0	0.15	0.52	2.63	4.8
14.0	0.32	0.52	2.63	11.0
14.0	0.55	0.52	2.63	18.3
14.0	0.92	0.52	2.63	21.1
14.0	1.17	0.52	2.63	28.7
14.0	1.48	0.52	2.63	41.5
14.0	0.74	0.22	2.63	23.3
14.0	0.74	0.34	2.63	20.0
14.0	0.74	0.52	2.63	22.0
14.0	0.74	0.65	2.63	18.7
14.0	0.74	0.17	0.70	31.1
14.0	0.74	0.17	1.17	23.2
14.0	0.74	0.17	1.63	15.8
14.0	0.74	0.17	2.56	14.9
14.0	0.74	0.17	3.48	15.0
14.0	0.74	0.17	4.08	28.2

^a See text. Reactions were carried out at 20 °C under N₂ atmosphere.

System A. A typical reaction profile is shown in Figure 1. The system, after a short induction time, rapidly reaches the maximum

- (1) (a) University of Venice. (b) CNR.
- (2) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047. Igersheim, F.; Mimoun, H. *Nouv. J. Chim.* **1980**, *4*, 711. Bregeault, J.-M.; Mimoun, H. *Nouv. J. Chim.* **1981**, *5*, 287. Roussel, M.; Mimoun, H. *J. Org. Chem.* **1980**, *45*, 5381.
- (3) 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.
- (4) Strukul, G.; Michelin, R. A.; Orbell, J. D.; Randaccio, L. *Inorg. Chem.* **1983**, *22*, 3706.
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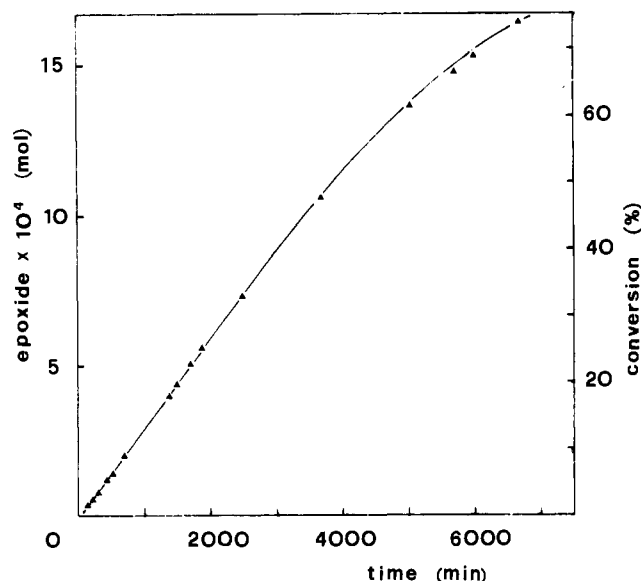


Figure 1. Epoxide formed vs time plot relative to system A. Reaction conditions: Pt_T , 4.20×10^{-5} mol; 1-octene, 2.23×10^{-3} mol; H_2O_2 , 1.95×10^{-3} mol; H_2O , 7.94×10^{-3} mol; THF, 2.46 mL. Conversions were calculated on the basis of 1-octene consumed.

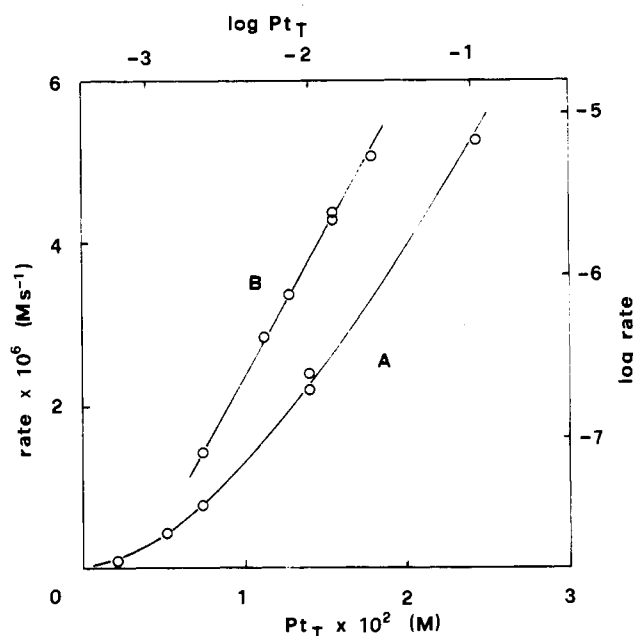


Figure 2. System A: effect of the total platinum concentration on the reaction rate. A: normal plot. B: log-log plot.

rate, which is maintained for a rather long interval (about 5–30% olefin conversion or about 10–40% H_2O_2 consumption) and therefore can be analyzed precisely. A summary of the kinetic data for system A is reported in Table I, and their analysis as a function of platinum, H_2O_2 , 1-octene, and H_2O concentrations is shown in Figures 2–5.

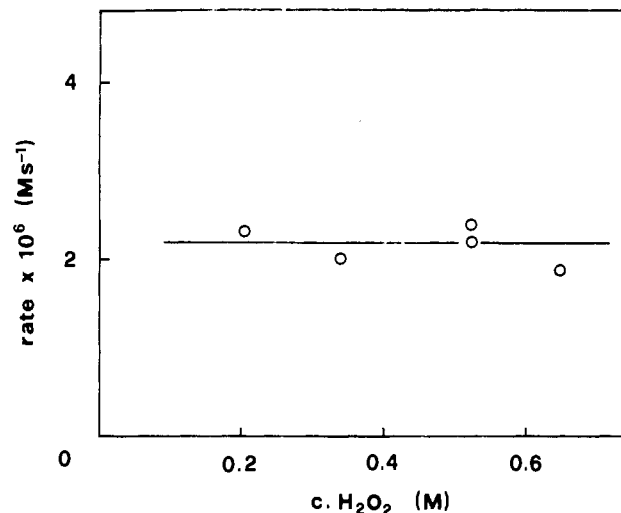


Figure 3. System A: effect of the concentration of H_2O_2 on the reaction rate.

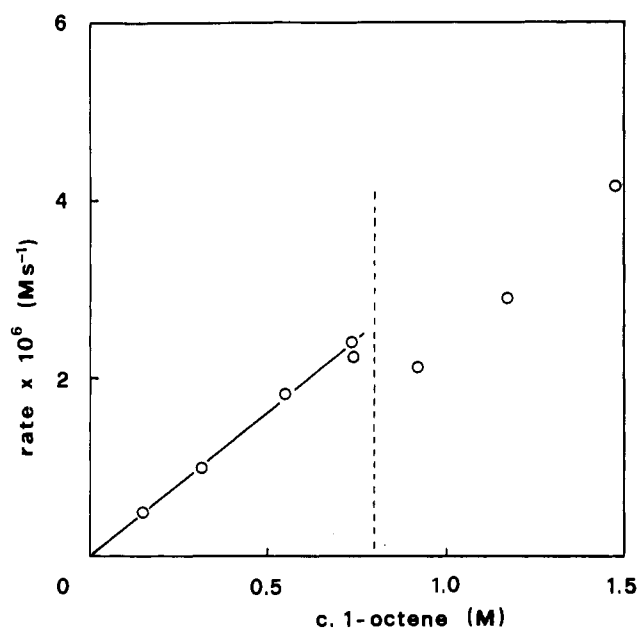


Figure 4. System A: effect of the concentration of 1-octene on the reaction rate.

Effects of Platinum and Hydrogen Peroxide. As is clear from Figure 2A and the corresponding log-log plot (Figure 2B), the dependence of the maximum rate on (diphoe) $\text{Pt}(\text{CF}_3)(\text{OH})$ concentration is second order.

As shown in Figure 3, the system is independent of H_2O_2 concentration.

Effects of 1-Octene and Water. Figures 4 and 5 report the dependence of the maximum rate on 1-octene and H_2O concentrations, respectively. In both cases the plots are divided into two regions. For concentrations higher than the broken line, the reaction medium separates into two phases, and therefore the kinetic data obtained are meaningless. For lower concentrations, the dependences of 1-octene and water are first order and inverse order, respectively. Unfortunately, in the latter case the range that could be explored was very limited, the minimum water concentration being that corresponding to the undiluted 34% H_2O_2 .

^{19}F NMR Experiments. Step-by-step ^{19}F NMR spectra have been carried out on the working catalytic system in order to obtain some information on the distribution of the platinum species macroscopically involved. Addition of 1-octene (0.1 mL) to (diphoe) $\text{Pt}(\text{CF}_3)(\text{OH})$ (50 mg) in CD_2Cl_2 (0.6 mL) (δ -27.40, $^3J_{\text{F-P}_{\text{cis}}} = 9.1$ Hz, $^3J_{\text{F-P}_{\text{trans}}} = 56.7$ Hz, $^2J_{\text{F-Pt}} = 596$ Hz) produces no variations. When 35% H_2O_2 (0.01 mL) is added, the full formation of a new species is observed (δ -27.32, $^3J_{\text{F-P}_{\text{cis}}} = 11.0$

- (6) Strukul, G.; Michelin, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 7563.
- (7) See for example: Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5832 and references therein.
- (8) Although there is a wide acceptance⁹ on the roles of the olefin and the hydroperoxide in d^0 -metal-mediated alkene oxidations as indicated in Scheme I, a recent report¹⁰ seems to suggest that the roles may be inverted.
- (9) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981; and references therein.
- (10) Mimoun, H.; Mignard, M.; Brechot, P.; Saussine, L. *J. Am. Chem. Soc.* **1986**, *108*, 3711.
- (11) Sheldon, R. A. *Aspects Homogeneous Catal.* **1981**, *4*, 3.
- (12) Sinigalia, R.; Michelin, R. A.; Pinna, F.; Strukul, G. *Organometallics* **1987**, *6*, 728.

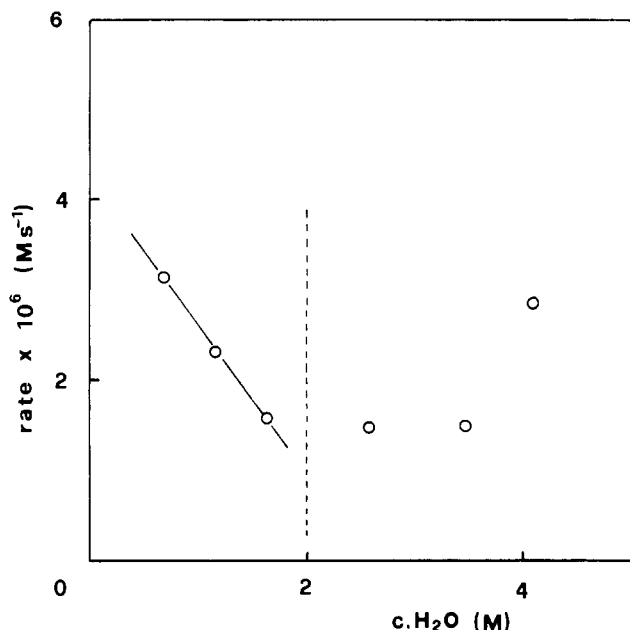
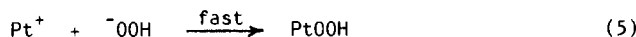
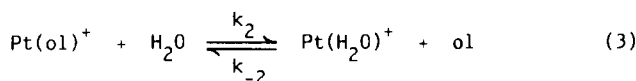
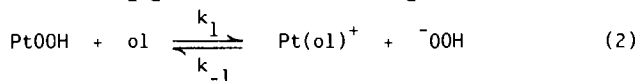
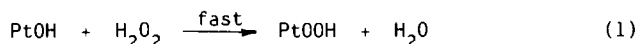


Figure 5. System A: effect of the concentration of H_2O on the reaction rate.

Scheme II



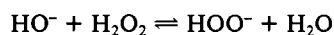
Hz, $^3J_{\text{F-Pt}} = 62.0$ Hz, $^2J_{\text{F-Pt}} = 554$ Hz), which is recognized to be (diphoe)Pt(CF₃)(OOH) by comparison with an authentic sample.¹³

Kinetic Scheme and Rate Law. The kinetic scheme reported in Scheme II accounts for the experimental observations so far reported.

¹⁹F NMR experiments indicate that the total platinum present is PtOOH only. Hence, a stationary-state approximation applied to reaction 4 implies that the Pt(ol)⁺ (ol = olefin) concentration is constant. Under these approximations the rate expression is

$$\frac{d[\text{epox}]}{dt} = \frac{k_1 k_3 [\text{Pt}]_T^2 [\text{ol}]}{k_{-1} [\text{HOO}^-] + k_2 [\text{H}_2\text{O}] + k_3 [\text{Pt}]_T}$$

where [Pt]_T represents the total concentration of all the platinum species present in the system and equals the concentration of starting complex introduced and the various concentrations are the initial concentrations. The expression is in good qualitative agreement with the experimental observations, assuming that $k_{-1}[\text{HOO}^-]$ and $k_3[\text{Pt}]_T$ are always negligible in the water concentration range explored. To test the incidence of $k_{-1}[\text{HOO}^-]$ on the reactivity, we also carried out a set of experiments where known amounts of HO⁻, which is related to HOO⁻ by the equilibrium



were added to the reaction medium. The results are summarized in Table II, where it appears that HO⁻ has a pronounced inhibitory

Table II. Effect of Added HO⁻ and H⁺ on the Reaction Rate in System A^a

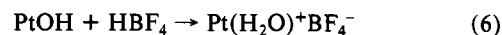
[HO ⁻] added, M	[H ⁺] added, M	10 ⁷ (rate), M s ⁻¹
10 ⁻³		3.7
10 ⁻⁵		5.2
10 ⁻⁶		6.1
10 ⁻⁷		7.5
0	0	18.7
	2 × 10 ⁻³	310
	4 × 10 ⁻³	421
	7 × 10 ⁻³	184
	1 × 10 ⁻²	13.5
	5 × 10 ⁻²	1.1
	1 × 10 ⁻¹	<0.1

^a See text. Reaction conditions [Pt]_T = 1.40 × 10⁻² M; [1-octene] = 0.74 M; [H₂O₂] = 0.65 M; [H₂O] = 2.63 M; T = 20 °C; N₂ atmosphere.

effect even for 10⁻⁷ M HO⁻ added. If one considers that commercial hydrogen peroxide is slightly acidic (pH ~ 3) because of H₂SO₄ impurities, it is clear that additions of HO⁻ to less than 10⁻⁵ M change the original HO⁻ concentration very little. These observations suggest that k_{-1} must be very large, and this is in agreement with previous basicity measurements carried out on (diphoe)Pt(CF₃)(OH),⁶ which appeared to be a poor base.

Evidence for the feasibility of reaction 4 was found in an especially designed separate experiment. Two equimolar solutions (10⁻² M in CH₂Cl₂) of [(diphoe)Pt(CF₃)(1-oct)]BF₄ (1-oct = 1-octene) and (diphoe)Pt(CF₃)(OOH) were prepared. These were mixed together, and the resulting solution was analyzed immediately with GLC, which indicated complete formation of 1,2-epoxyoctane. The complex was isolated and recognized to be (¹⁹F NMR evidence) a mixture of [(diphoe)Pt(CF₃(CH₂Cl₂)]⁺ (see below for NMR parameters) and (diphoe)Pt(CF₃)(OH).¹⁴ It has to be pointed out that, according to previous observations,¹³ free 1-octene is unreactive toward (diphoe)Pt(CF₃)(OOH) in anhydrous media. Unfortunately, the above stoichiometric reaction, which would be very informative for the overall catalytic systems, cannot be studied kinetically since it is too fast for GLC measurements. Moreover, UV-vis techniques are useless because the spectra of the complexes (starting and final) are featureless and the differences in absorption are very poor.

Effect of Added Acid. The latter experiment seems to suggest that the catalytic ability of the system might be significantly increased if an appropriate balance of Pt(ol)⁺ and PtOOH species is operative in the reaction mixture. It is known^{6,15} that many hydroxo complexes of Pt(II) of the type here used can be easily converted to the corresponding aquo complexes by addition of strong noncoordinating acids according to reaction 6. Clearly,



H₂O can be displaced by olefins much more easily than HOO⁻, as is required in reaction 2 of Scheme II. Therefore, we have added increasing amounts of perchloric acid to the catalytic system and have measured the corresponding epoxidation rates. The dramatic effect shown in Figure 6 is observed where the effect of added base is also shown: starting from no acid or base added, where PtOOH largely predominates, the reaction rate increases rapidly to reach a maximum for H⁺ added corresponding to about 30% of the platinum present (1.4 × 10⁻² M), where the best balance between Pt(ol)⁺ and PtOOH is attained, and then rapidly decreases when the PtOOH species becomes almost completely protonated.

Attempts to computer-analyze the kinetic data with a multivariate nonlinear regression of rate vs [Pt]_T, [ol], and [H₂O] by an improved version of Marquardt's method¹⁶ proved meaningless

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

(16) Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *2*, 431. Campagnaro, A.; Mantovani, A.; Uguagliati, P. *Inorg. Chim. Acta* **1985**, *99*, L15 and references therein.

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

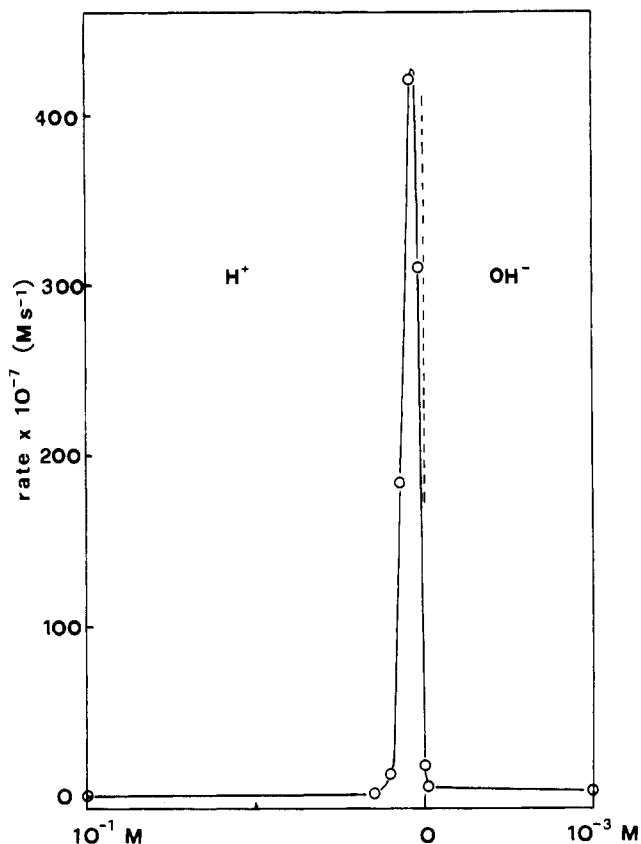


Figure 6. System A: effect of the addition of H^+ and OH^- on the reaction rate.

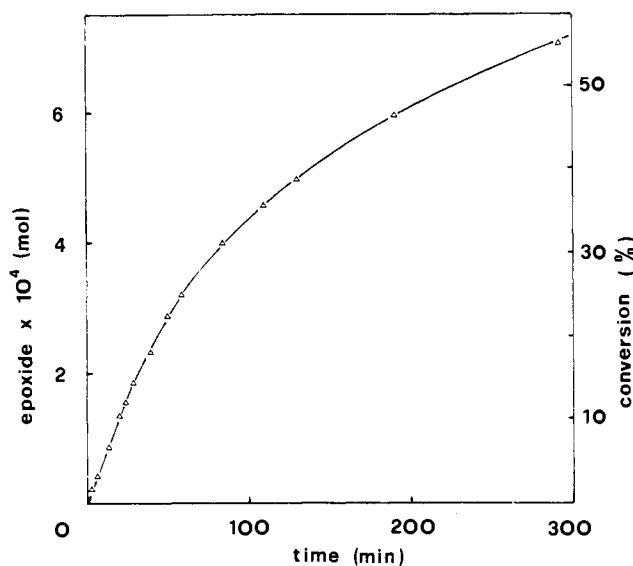


Figure 7. Epoxide formed vs time plot relative to system B. Reaction conditions: Pt_T , 2.55×10^{-5} mol; 1-octene, 1.28×10^{-3} mol; H_2O_2 , 4.61×10^{-3} mol; CH_2Cl_2 , 12.6 mL. Conversions were calculated on the basis of 1-octene consumed.

because of the complexity of the system and the narrowness of some concentration ranges that could be objectively analyzed (see Figures 4 and 5).

System B. The same set of experiments was carried out on system B. A typical reaction profile is reported in Figure 7, where it appears that the plot is linear for an initial short (15–40 min) interval where the maximum rate is also observed. This initial rate can be conveniently analyzed as a function of the concentrations of the individual reactants, and a summary of the kinetic data is reported in Table III. It has to be pointed out that, for initial rates of about $1.4 \times 10^{-4} M s^{-1}$ or more, the reaction starts becoming controlled by the diffusion of H_2O_2 from the aqueous

Table III. Summary of Kinetic Data Relative to System B^a

$10^4 Pt_T$, M	[1-octene], M	$10^3 [H_2O_2]_{org}$, M ^b	$10^6 (rate)$, M s ^{-1 c}
2.8	1.39	8.12	1.9 (0.4)
4.7	1.39	8.12	4.4 (2.0)
8.5	1.39	8.12	8.8 (8.6)
11.3	1.39	8.12	13
16.0	1.39	8.12	20 (31)
16.6	1.39	8.12	33 (31)
21.8	1.39	8.12	46 (48)
28.2	1.39	8.12	85 (87)
32.9	1.39	8.12	121 (108)
20.0	0.40	0.81	2.6
20.0	0.40	1.62	5.7
20.0	0.40	3.24	9.7
20.0	0.40	4.88	16
20.0	0.40	8.12	21
20.0	0.40	12.1	25
20.0	0.40	16.2	26
20.0	0.024	8.12	2.5
20.0	0.050	8.12	3.9
20.0	0.10	8.12	8.3
20.0	0.15	8.12	13.6
20.0	0.30	8.12	25.5
20.0	0.60	8.12	37.8
20.0	0.99	8.12	47.5
20.0	1.39	8.12	56.0

^aSee text. Reactions were carried out at 20 °C under N_2 atmosphere. ^bConcentration in the organic phase determined according to ref 9. ^cNumbers in parentheses refer to systems where the aqueous phase was buffered with hydrosulfate at pH 1.6.

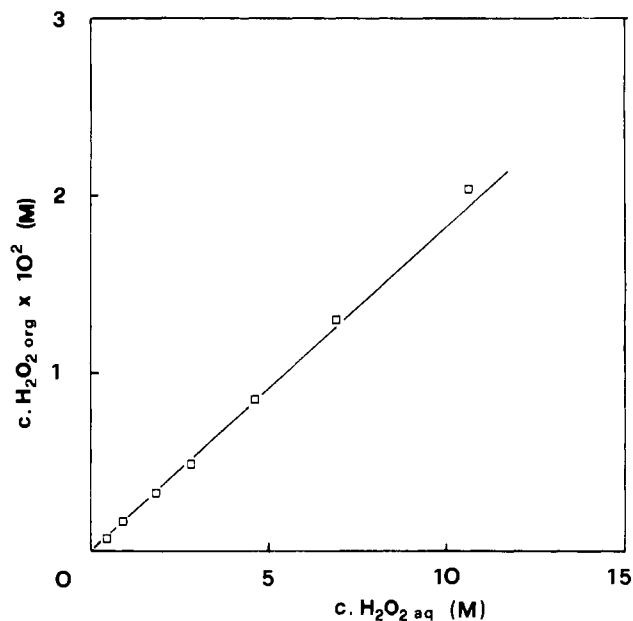


Figure 8. Plot of the concentration of H_2O_2 in CH_2Cl_2 vs concentration of H_2O_2 in the aqueous phase.

to the organic phase (see Experimental Section), and therefore in this range, even if vigorous stirring is applied, reliable data cannot be obtained.

Since the reaction medium is biphasic, the actual concentration of H_2O_2 in the organic phase was determined spectrophotometrically with Ti^{4+} according to the method described by Wolfe.¹⁷ A plot of $[H_2O_2]_{org}$ vs $[H_2O_2]_{aq}$ is reported in Figure 8.

The data of Table III are reorganized in Figures 9–11, where the effects of platinum, 1-octene, and H_2O_2 are shown.

Effects of 1-Octene and H_2O_2 . Figures 9 and 10 clearly indicate the similar behavior of the system reaction rates as a function of 1-octene and H_2O_2 concentrations. In both cases the dependence is initially linear and tends to become zero order for higher concentrations.

(17) Wolfe, W. C. *Anal. Chem.* 1962, 34, 1328.

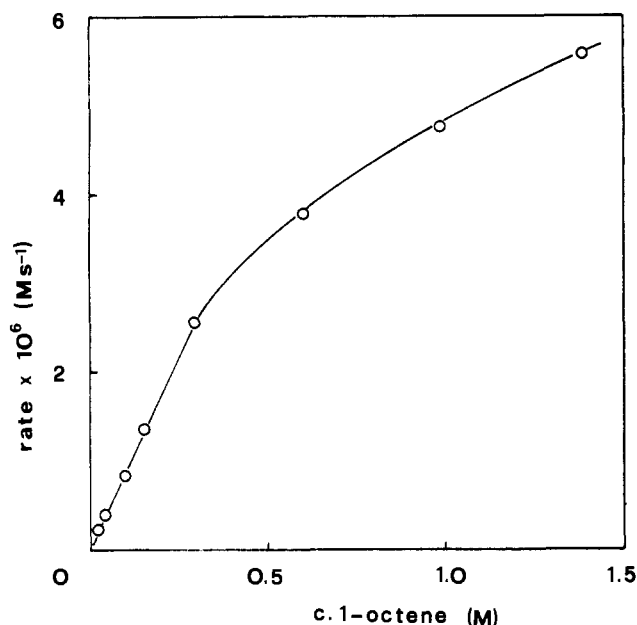


Figure 9. System B: effect of the concentration of 1-octene on the reaction rate.

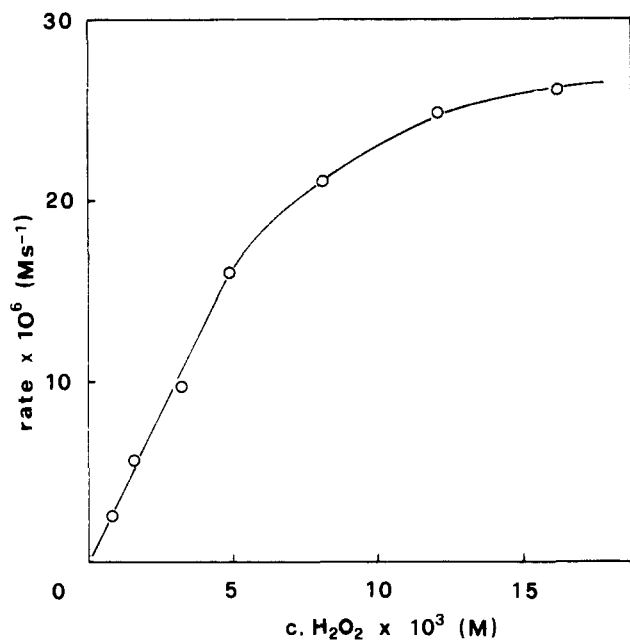


Figure 10. System B: effect of the concentration of H_2O_2 on the reaction rate.

Effect of Platinum. As it appears from Figure 11A (squares), the relationship between rate and platinum concentration is complex and seems to indicate again a second-order dependence. This observation suggests that a PtOOH species is again involved as the oxidant, probably formed according to reaction 10 of Scheme III, which requires the formation of H^+ . This has been checked by pH measurements for a catalytic run containing $[\text{Pt}] = 2.0 \times 10^{-3} \text{ M}$. The 17% H_2O_2 solution (pH 3.6) was injected into the catalytic system, and after ~ 20 min the resulting pH was 2.0. Moreover, concentration of the organic phase followed by addition of Et_2O resulted in the precipitation of a solid that, upon analysis with solution (CH_2Cl_2) IR spectroscopy, showed a band maximum at 3520 cm^{-1} , typical of $(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{OOH})$.¹³ Since H^+ is involved in the catalysis, the data in Table III should be recalculated at constant pH. However, the pH variation in the system was found to be modest (about 0.2 unit) when either the H_2O_2 or the 1-octene concentrations are changed in the two ranges considered. Therefore we recalculated only the effect of platinum concentration at constant pH. Hydrosulfate

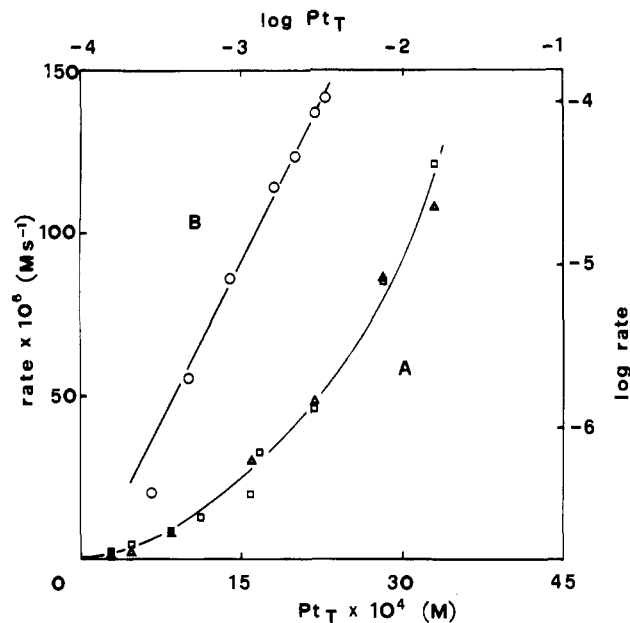


Figure 11. System B: effect of the total platinum concentration on the reaction rate: (A) normal plot (unbuffered, squares; buffered, triangles); (B) log-log plot (buffered).

buffers (pH 2.0) changed significantly in acidity (pH 1.6) when diluted 1/1 with 34% H_2O_2 . However, since the buffering ability was retained, the apparent change in pH is probably due to solvent effects due to the fact that the H_2O medium contains 17% H_2O_2 . The effect of platinum was recalculated by using H_2O_2 solutions buffered at apparent pH 1.6. The corresponding initial rate data are reported in Table III and Figure 11A (triangles), where significant differences with the unbuffered experiments can be observed at lower Pt concentrations. A second-order dependence is again evident from Figure 11A (triangles), which was confirmed by the log-log plot (Figure 11B).

^{19}F NMR Experiments. Again, step-by-step ^{19}F NMR spectra have been carried out on the working catalytic system. The spectrum of the initial $[(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{CH}_2\text{Cl}_2)]\text{BF}_4$ complex (50 mg) in CD_2Cl_2 (0.6 mL) consists of two broad signals with Pt satellites centered around $\delta -28.58$. This spectrum, which is clearly fluxional at room temperature, becomes static at -70°C , where all the coupling constants can be easily determined ($\delta -29.36$, $^3J_{\text{F-Pt}_{\text{cis}}} = 8.6 \text{ Hz}$, $^3J_{\text{F-Pt}_{\text{trans}}} = 56.7 \text{ Hz}$, $^2J_{\text{F-Pt}} = 518 \text{ Hz}$). Addition of 1-octene (0.1 mL) at room temperature produces a new species ($\delta -21.07$, $^3J_{\text{F-Pt}_{\text{cis}}} = 14.3 \text{ Hz}$, $^3J_{\text{F-Pt}_{\text{trans}}} = 57.4 \text{ Hz}$, $^2J_{\text{F-Pt}} = 517 \text{ Hz}$), which again is slightly fluxional. The new Pt-olefin complex and the previous Pt-solvent species are both present, and from integration data a formation constant of about 3.0 can be estimated. Then 34% H_2O_2 (0.01 mL) was added. The new spectrum shows again the presence of $[(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{CH}_2\text{Cl}_2)]\text{BF}_4$, extensive broadening of the signals corresponding to $[(\text{diphoe})\text{Pt}(\text{CF}_3)(1\text{-oct})]\text{BF}_4$, and the appearance of a third major species ($\delta -27.43$, $^3J_{\text{F-Pt}_{\text{cis}}} = 9.6 \text{ Hz}$, $^3J_{\text{F-Pt}_{\text{trans}}} = 57.9 \text{ Hz}$, $^2J_{\text{F-Pt}} = 542 \text{ Hz}$). In order to identify this third species, we carried out two separate experiments where 34% H_2O_2 and H_2O were separately added to a solution of $[(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{CH}_2\text{Cl}_2)]\text{BF}_4$ in CD_2Cl_2 . The two ^{19}F NMR spectra obtained were identical and showed the presence of the same species obtained in the catalytic experiment. Since the above reported pH and IR experiments indicated the presence of significant amounts of $(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{OOH})$ ($\delta -27.32$, $^3J_{\text{F-Pt}_{\text{cis}}} = 11.0 \text{ Hz}$, $^3J_{\text{F-Pt}_{\text{trans}}} = 62.0 \text{ Hz}$, $^2J_{\text{F-Pt}} = 554 \text{ Hz}$), we conclude that the third major species observed in the catalytic experiment is most likely a mixture of $[(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{H}_2\text{O})]\text{BF}_4$, $[(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{H}_2\text{O}_2)]\text{BF}_4$, and $(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{OOH})$, giving rise to practically undistinguishable ^{19}F NMR spectra.

Kinetic Scheme and Rate Law. On the basis of the results so far obtained, we suggest for the catalytic reaction the kinetic scheme shown in Scheme III.

Scheme III

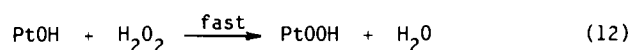
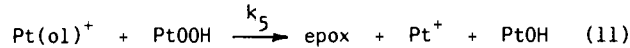
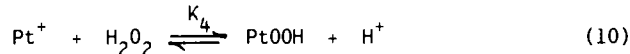
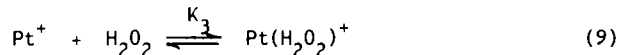
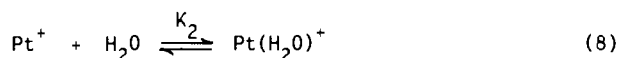
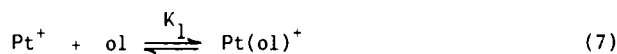


Table IV. Effect of the pH of the Aqueous Phase on the Catalytic Activity in System B^a

pH	10 ⁶ (rate), M s ⁻¹	pH	10 ⁶ (rate), M s ⁻¹
0.7	7.4	4.4	73.5
1.3	8.5	4.7	65.0
1.9	11.6	5.0	57.4
2.1	12.0	5.3	39.9
2.3	14.0	5.9	30.0

^aSee text. Reaction conditions in the range pH 0.7–2.3 with hydrosulfate buffer: [Pt]_T = 20.0 × 10⁻³ M; [1-octene] = 0.3 M; [H₂O₂]_{org} = 4.06 × 10⁻³ M; T = 20 °C; N₂ atmosphere. Reaction conditions in the range pH 4.4–5.9 with phosphate buffer: [Pt]_T = 20.0 × 10⁻³ M; [1-octene] = 1.39 M; [H₂O₂]_{org} = 8.12 × 10⁻³ M; T, 20 °C; N₂ atmosphere.

Since the ¹⁹F NMR spectra have been carried out with olefin and H₂O₂ concentrations that are in the same range of those involved in the catalytic experiments, while platinum concentration was about 50–500 times higher, none of the platinum species of Scheme III can be neglected, and the rate expression becomes

$$\frac{d[\text{epox}]}{dt} = \frac{k_5 K_4 K_6 \times [\text{Pt}]_T^2 [\text{ol}] [\text{H}_2\text{O}_2]}{[\text{H}^+] (1 + K_1 [\text{ol}] + K_2 [\text{H}_2\text{O}] + K_3 [\text{H}_2\text{O}_2] + K_4 [\text{H}_2\text{O}_2] / [\text{H}^+])^2}$$

where [Pt]_T represents the total platinum concentration introduced and the various concentrations are the initial concentrations. This is in good qualitative agreement with the individual concentration dependences shown in Figures 9–11, assuming that in the ranges explored [ol] and [H₂O₂] are never sufficiently high to display inverse dependence as would be predicted by the rate law.

Since the H⁺ concentration in the organic phase was not known, we did not try any computer analysis.

Effect of pH. The rate expression predicts a complex dependence of the catalytic system on pH, again reflecting the balance between Pt⁺ and PtOOH concentrations determined by reaction 11. So, from low to high pH values, the rate would be initially increasing, then passing through a maximum, and finally decreasing, analogous to the effect observed for system A. The apparent pH of the aqueous phase was changed at lower values with hydrosulfate buffers and at higher values with phosphate buffers. The corresponding rates are shown in Table IV and Figure 12. It has to be pointed out that, although sulfate and phosphate are generally considered as "noncoordinating" anions, a certain interaction with coordinatively unsaturated cationic species is to be expected; the extent of this interaction will be different in the two cases, and therefore the data obtained with hydrosulfate buffers can be compared only qualitatively to those obtained with phosphate buffers since they refer to different reactions conditions. Within this limitation, the results shown in Figure 12 are in good qualitative agreement with the rate expression. Unfortunately, we could not cover the pH range 2.4–4.4, where the maximum rate should be observed, since all the buffers tested (oxalate, tartrate, acetate) strongly inhibit the catalytic activity.

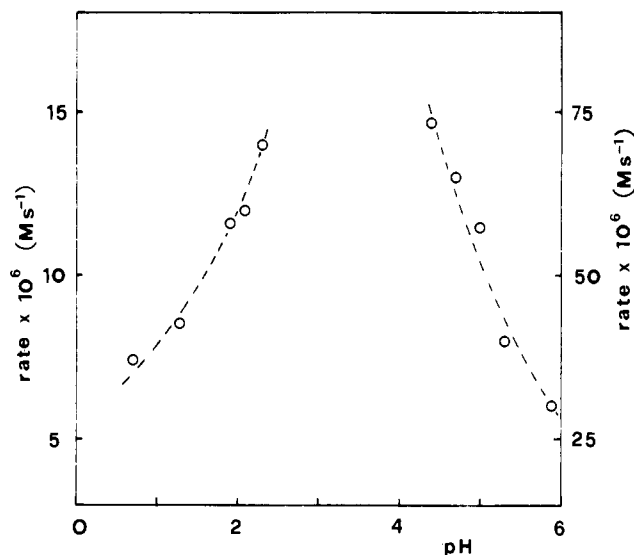


Figure 12. System B: effect of pH on the reaction rate.

Discussion

A first general comment on the reliability of the mechanisms formulated in Schemes II and III arises from the fact that they not only complement each other and are mutually supporting but also, from the large body of qualitative evidences intrinsic in the fact, that most of the steps involved have been separately and individually observed.

A comparison of the kinetic data reported in Table I with those of Table III clearly indicates that the efficiency with which the Pt-olefin complex is formed is the factor most critical to the achievement of high reaction rates, while the oxidant ability of (diphoe)Pt(CF₃)(OOH) must be very high since the maximum rates are observed in system B, where it forms in lower concentrations. As the pH effect has demonstrated both in system A and in system B, there exists an optimum balance between Pt(ol)⁺ and PtOOH where the maximum rates can be achieved.

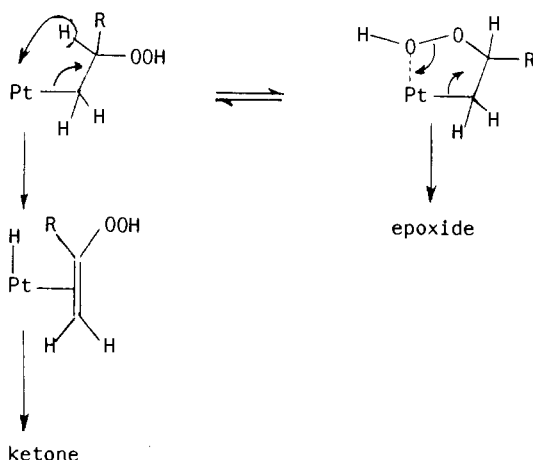
The results of this kinetic study appear to indicate the PtOOH species as the exclusive oxidant in the catalytic system. In generalizing this conclusion to other active homologous complexes, one must consider the stability of the corresponding hydroperoxo species, which was found to vary widely depending on the ancillary phosphine and alkyl ligands.¹³ In some cases it is quite possible that H₂O₂ itself may be involved as the oxidant, especially for the cationic complexes, where the PtOOH species forms in lower concentrations.

In its basic mechanistic features the present system bears strong similarities to the Wacker process,^{9,18} particularly as far as the oxygen transfer is concerned. In fact, mechanistic studies have shown^{19,20} that the so-called hydroxypalladation is actually a bimolecular process, proceeding with external nucleophilic attack of water on the coordinated olefin and leading to trans insertion products. It is significant that, when the present system modified with chiral diphosphines has been successfully employed in the asymmetric epoxidation of olefins,¹² the assumption of a trans stereochemistry in the oxygen-transfer step has been a key choice for the rationalization of the optical purity data.

The results reported above provide the first direct evidence of the involvement of two individual metal species in the oxygen transfer from a metal peroxo to a metal olefin species, the only precedent being the recently observed oxidation of a Pt-CO moiety

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Scheme IV



by a PtO₂ side-bonded peroxy species reported by Kubota et al.²¹ Moreover, Mares and co-workers²² have recently indirectly demonstrated the involvement of both an olefin-Pd(II) complex and a nitro-Co(III) species in the oxygen-transfer step of their bimetallic catalytic oxidation system.²³ Although the latter does not involve peroxides, it does show some mechanistic similarities to the present platinum system. The fact that two individual metal species are involved in the oxygen transfer illustrates directly the first point set forth in the Introduction, i.e., the bifunctional role of platinum, which, on the one hand, enhances olefin reactivity by making it susceptible to nucleophilic attack and, on the other hand, increases H₂O₂ nucleophilicity through coordination of a formal HOO⁻ ligand. The partial ionic character of the Pt-O bond in a series of hydroxo, hydroperoxy, and *tert*-butylperoxy complexes of Pt(II) has been previously demonstrated by us with NMR spectroscopy.⁴ Clearly, this bifunctional role, which is not formal but is substantial, can be more easily performed by involving two individual metal species rather than by coordinating both reactants on the same metal center, where the two effects might be averaged.

The reactivity pattern that emerges from the observations described in the present study is very similar to the well-known nucleophilic behavior of the (PPh₃)₂PtO₂ side-bonded peroxy complex with respect to a series of electrophiles such as acids,²⁴ alkyl halides,⁷ ketones, and aldehydes.²⁵ The consequence of the above consideration is that, compared to the case of d⁸-metal-based oxidations, in this system the role of the electrophile and that of the nucleophile are inverted, as we have stated in the Introduction.

Of the two roles performed by platinum complexes in the present system, oxidant and olefin activator, the former appears to be rather peculiar, while as far as the latter is concerned, in principle, Pt(II) might be more conveniently substituted with systems capable of promoting nucleophilic attack more efficiently, for example Pd(II).²⁶ However, it must be pointed out that another characteristic of the present system is the unusual nature

of the oxidation product, i.e. epoxide, at variance with other group VIII transition-metal-based systems.^{2,3,27} We have suggested⁶ from some indirect observations that this may arise from the formation of a quasi-peroxymetallacycle (Scheme IV) favored by steric reasons, coupled with the less pronounced tendency of platinum to undergo β-hydride addition-eliminations, which by analogy with the mechanism proposed by Andrews for metal-nitro complexes²⁸ may be responsible for the formation of ketones. Unfortunately the kinetic experiments do not give any indication from this point of view, and therefore the incidence of the chemistry described in Scheme IV needs to be further substantiated in some other way.

Experimental Section

Apparatus. IR spectra were taken on a Perkin-Elmer 597 spectrophotometer either in Nujol mulls (CsI plates) or in solution (NaCl windows). Solution UV-vis spectra were recorded on a Cary 219 spectrophotometer. ¹⁹F NMR spectra were recorded on a Varian FT 80A spectrometer operating in FT mode with an external reference of CFC₃. Negative chemical shifts are upfield from the reference. GLC measurements were taken on a Hewlett-Packard 5890A gas chromatograph equipped with a Hewlett-Packard 3390A integrator. Identification of products was made with GLC by comparison with authentic samples. Computer analysis of the kinetic data was performed on a Tektronix 4052 graphic system.

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 (34%) (Fluka) was a commercial product and was used without purification. The preparation of the complexes was performed under dry N₂ by conventional Schlenk and syringe techniques.

The following compounds were prepared by literature methods: (diphoe)Pt(CF₃)Cl,¹⁴ (diphoe)Pt(CF₃)(OH),¹⁴ [(diphoe)Pt(CF₃)(CH₂Cl₂)]BF₄,¹⁴ (diphoe)Pt(CF₃)(OOH),¹³ and 1,2-epoxyoctane.²⁹

[(diphoe)Pt(CF₃)(1-oct)]BF₄, (diphoe)Pt(CF₃)Cl (0.20 g, 0.29 mmol) was dissolved in N₂-saturated CH₂Cl₂ (15 mL). A solution of AgBF₄ (0.29 mL, 1.0 M in acetone) was added dropwise with stirring. After 30 min, AgCl was filtered off, and to the clear solution was added 1-octene (3 mL). The solution was slowly evaporated in vacuo until precipitation of a white solid, which was filtered out, washed with heptane, and dried in vacuo (yield 87%). ¹⁹F NMR at -70 °C: -29.36 ppm (dd), ³J_{F-Pt} = 8.6, ³J_{F-trans} = 56.7, ²J_{F-Pt} = 518.

Reaction between [(diphoe)Pt(CF₃)(1-oct)]BF₄ and (diphoe)Pt(CF₃)(OOH). [(diphoe)Pt(CF₃)(1-oct)]BF₄ (42.9 mg, 0.05 mmol) and (diphoe)Pt(CF₃)(OOH) (34.7 mg, 0.05 mmol) were separately dissolved in CH₂Cl₂ (5 mL). The two solutions were mixed together under N₂ with the aid of a syringe. After the mixture was stirred for a few seconds, the resulting solution was sampled and analyzed with GLC, indicating complete formation of 1,2-epoxyoctane. The solution was concentrated in vacuo to ~3 mL, and Et₂O (10 mL) was added. The white solid obtained was filtered off, washed with Et₂O, dried in vacuo, and analyzed by ¹⁹F NMR spectroscopy.

Determination of H₂O₂ Concentration in CH₂Cl₂. This was performed according to a modified procedure of the method described by Wolfe.¹² To a typical blank reaction mixture (10 mL of CH₂Cl₂ + 2.8 mL of 1-octene) was added 1.0 mL of aqueous H₂O₂ of known concentration. After stirring of the mixture for a few minutes, a 10-mL portion of the organic phase was separated. To this was added an equal amount of H₂O, and after this mixture was stirred for a few minutes, a 5-mL aliquot of the aqueous phase was separated and diluted to 25 mL with a 2.1 M solution of TiCl₄ in 6 N HCl to give an orange solution. Spectrophotometric analysis was carried out at 418 nm (ε 741). The Lambert-Beer law was obeyed in the concentration range explored.

Rate Studies. 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 ± 0.1 °C) was maintained by water circulation through an external jacket connected with a thermostat. Stirring was performed

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by a Teflon-coated bar driven externally by a magnetic stirrer. Absence of diffusional problems below $1.4 \times 10^{-4} \text{ M s}^{-1}$ initial rates was determined by the conversion vs time plot independence of the stirring rate in kinetic experiments randomly selected from Table II. Possible phase separation in the case of system A was checked with UV-vis spectroscopy by analyzing blank solutions (without catalyst) at 350 nm. The concentration of the commercial H_2O_2 solution was checked iodometrically prior to use.

The following general procedures were followed:

System A. In a typical experiment solid (diphoe)Pt(CF₃)(OH) (0.0284 g, 0.042 mmol) was placed in the reactor, which was evacuated and filled with N₂. Dry, N₂-saturated THF (2.5 mL) was added under N₂ flow, followed by 1-octene (0.350 mL, 2.23 mmol). After stirring of the mixture for a few minutes, a 34% H_2O_2 solution (0.190 mL, 1.80 mmol) was injected through the septum and time was started. The mixture was vigorously stirred to avoid diffusional problems. Where necessary, appropriate amounts of water, HClO_4 , or KOH were added to the H_2O_2 solution prior to use.

System B. The sequences of operations was analogous to system A except that the amounts used were different. Typically, the following

compounds and amounts were used: [(diphoe)Pt(CF₃)(CH₂Cl₂)]BF₄ (0.0215 g, 0.026 mmol), CH₂Cl₂ (10 mL), 1-octene (2.80 mL, 17.8 mmol), 17% H_2O_2 (1.0 mL, 5.0 mmol). In buffered experiments the buffer solution was diluted 1/1 with 34% H_2O_2 prior to use.

All reactions were monitored with GLC by direct injection of samples taken periodically from the reaction mixtures with a microsyringe. Prior quenching of the catalyst with LiCl did not show any differences in randomly selected analyses. Separation of the products was performed on a 2-m 10% UCC on Chromosorb W packed column by using a flame ionization detector.

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Registry No. (diphoe)Pt(CF₃)(OH), 70504-87-9; [(diphoe)Pt(CF₃)(CH₂Cl₂)]BF₄, 98839-55-5; 1-octene, 111-66-0.

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Oxygen-17 Nuclear Magnetic Resonance Kinetic Study of Water Exchange on the Lanthanide(III) Aqua Ions^{1,2}

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We report a variable-temperature ¹⁷O NMR study of aqueous lanthanide solutions. Chemical shift measurements on 0.3 *m* Ln(ClO₄)₃/2 *m* HClO₄ solutions of 12 paramagnetic lanthanide ions are consistent with a constant hydration number along the series. This observation is reinforced by spectrophotometric measurements in acidified Nd(ClO₄)₃ solutions. A critical review of the previously published results on this topic suggests that the hydration number is nine for all lanthanide ions. The study was made on high-field NMR spectrometers, extending the accessible kinetic NMR window toward larger rate constants. By a combination of the chemical shifts and the longitudinal and the transverse relaxation rates, the water exchange activation parameters were obtained for six heavy lanthanide ions. The exchange rate constants calculated at 298.15 K are $5.0 \times 10^8 \text{ s}^{-1}$ for Tb³⁺, $3.9 \times 10^8 \text{ s}^{-1}$ for Dy³⁺, $1.9 \times 10^8 \text{ s}^{-1}$ for Ho³⁺, $1.2 \times 10^8 \text{ s}^{-1}$ for Er³⁺, $8.1 \times 10^7 \text{ s}^{-1}$ for Tm³⁺, and $4.1 \times 10^7 \text{ s}^{-1}$ for Yb³⁺. Unsuccessful attempts were made to study the water exchange on Nd³⁺ and Eu³⁺. The regular decrease of the k^{298} value with ionic radius and the fairly constant negative activation entropies are interpreted as grounds for a similar exchange mechanism for the six ions successfully kinetically characterized.

Introduction

The tripositive lanthanides constitute the longest series of chemically similar metal ions. As their 4f orbitals are shielded by the electrons of the filled 5s and 5p orbitals, ligand field effects or ligand π -orbital back-bonding are very weak. The stability and kinetic behavior of the lanthanide complexes are thus mainly governed by steric and electrostatic factors. The high coordination number and the absence of crystal field stabilization energy are responsible for the considerable lability of the lanthanide complexes.

The behavior of lanthanide(III) ions in aqueous solution remains quite an open question, and many papers concerning the hydration of these ions have already been published. However, as shown by Lincoln's recent review,³ it is not firmly established whether or not there is a change in coordination number (nine to eight) along the series.

Much has been published about complex formation on these ions, but knowledge of the water exchange kinetics is still very poor. Southwood-Jones et al.⁴ reported a variable temperature study of water exchange on Gd³⁺. For this ion, reliable kinetic characterization was made possible by a combination of ¹⁷O NMR

and EPR data. In an older ¹⁷O NMR study Reuben and Fiat,⁵ limited by the low magnetic field (1.4 T) then available, determined only lower limits for the water exchange rates at ambient temperature on the ions Tb³⁺ to Tm³⁺. As the chemical shift scale and the accessible NMR time scale are extended with an increase of magnetic field, we have performed a variable-temperature kinetic study with high-field (4.7 and 8.5 T) spectrometers. By combining the chemical shifts and the longitudinal and the transverse relaxation rates, we were able to characterize the water exchange kinetics on six heavy lanthanide ions. Moreover, the interpretation of the chemical shifts of water in paramagnetic lanthanide solutions and the results of spectrophotometric measurements gave us useful information about the coordination number of these ions in water.

Experimental Section

A. Materials and Solution Preparation. The lanthanide perchlorates were obtained by dissolving slight excesses of lanthanide oxides (Nucor, 99.99%; Apache Chemical, 99.9%) in 30% perchloric acid (Merck, p.a.). The resulting solutions were filtered and acidified to pH 3 with dilute HClO₄, in order to avoid the formation of hydroxo species, and were then evaporated at reduced pressure and the remaining solids were dried under vacuum. Further handling of these hygroscopic salts was always done in a dry glovebox. The hydration of the salts (6-8 mol of water/lanthanide ion) was calculated from the metal content, determined by titration with EDTA.⁶ Solutions were prepared by weight with 2 *m* HClO₄ as solvent, in order to avoid hydrolysis. Solutions for the spectrophotometric measurements were made with normal water, while those

(1) This work is part of the Ph.D. Thesis of C.C., University of Lausanne, 1986, and was presented at the 2nd International Conference on the Basic and Applied Chemistry of f-Transition and Related Elements, Lisbon, April 1987. A preliminary account of this work is given in the proceedings of the conference (see ref 2).

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