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Epoxidation of Olefins by Water Oxygen Catalyzed by Platinum Blue Complexes

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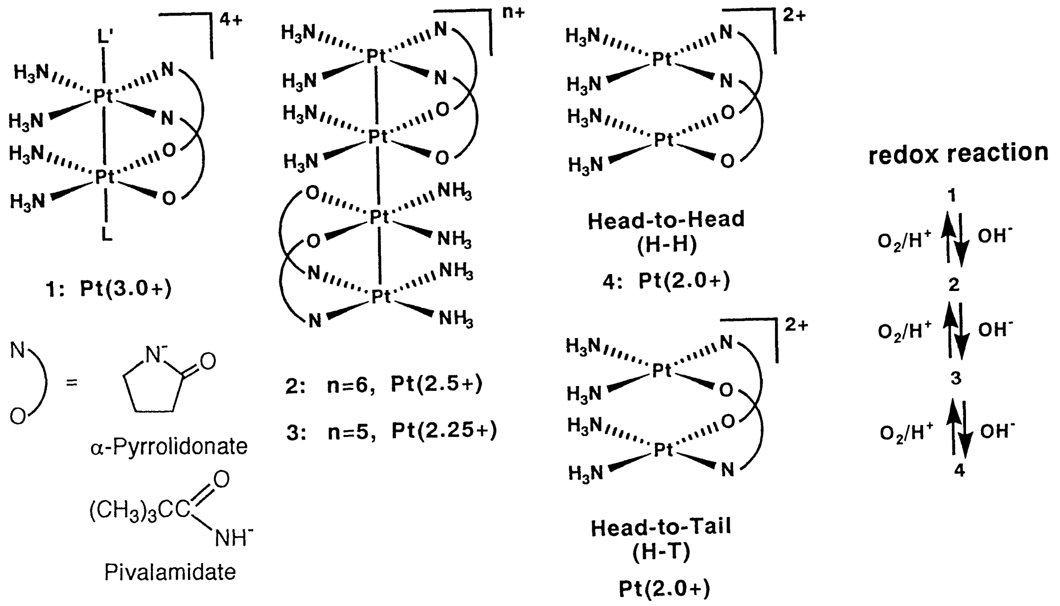
The first olefin epoxidation by water oxygen is reported. The reaction is catalyzed by platinum blue complexes and is the first example that water oxygen atom is introduced into epoxides in catalytic or stoichiometric reaction.

Oxidation of olefins to epoxides catalyzed by transition-metal complexes has extensively been studied, in one reason, for the mechanistic understanding of the biochemical oxygenation reactions catalyzed by metalloporphyrin enzymes,1-3) and in another, because of the importance of epoxides in industry.2,4) Olefin epoxidation by peroxides catalyzed by early transition metals proceeds, in most cases, via nucleophilic attack of the olefin onto the coordinated peroxidic oxygen.2,4,5) On the other hand, the use of more basic group VIII transition metal complexes in olefin oxidation leads almost invariably to ketonization.4,6) The only exception to date is $[Pt(diphoe)(CF_3)(X)]^{n+}$ (diphoe = cis-1,2-bis-(diphenylphosphino)ethane, X = CH_2Cl_2, OH^-, and n = 1, 0), which catalyzes selective formation of either epoxides or ketones, depending on the peroxides used.7-9) Amidate-bridged mixed-valent Pt(II)/Pt(III) compounds called "platinum blues"10-12) are reversibly oxidized by O_2 and reduced by OH^-, as shown in Scheme 1.13) These properties tempted us to use these compounds as the catalysts for olefin oxidation by O_2. What we have unexpectedly found in the present attempt is that cyclic olefins are selectively epoxidized by water oxygen, whereas linear terminal olefins are selectively ketonized.

Platinum blue10) and tan compounds,11,12) α-pyrrolidonate tan $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6\ 2H_2O$ (**1**) and pivalamidate blue $[Pt_4(NH_3)_8(C_5H_{10}NO)_4](NO_3)_5$ (**2**)14, were used as the catalysts. In a typical reaction, 10 μmole of the platinum complex and 5 (for **2**) or 6 (for **1**) equivalents of $C_{12}H_{25}SO_3Na$ as a surfactant were dissolved in a mixture of 1 mL of 0.05 M H_2SO_4 and 1 mL of CH_2ClCH_2Cl containing excess (~100 equivalents) olefin. The



Scheme 1.

Table 1. Olefin Oxidation Catalyzed by Platinum Blue Compounds

Substrate	Product	Turnover Number[a)] Catalyst 1	 2
1-heptene	2-heptanone[b)]	13.3	4.5
1-octene	2-octanone[b)]	15.8	12.4
1-decene	2-decanone	10.9	4.1
2-octene	2-octanone	1.7	1.6
	3-octanone	2.2	1.6
cyclohexene	cyclohexene oxide	22.8	15.0
	cyclohexanone[c)]	1.9	1.4
norbornene	norbornene oxide	7.2	5.2
	norbornanone[d)]	2.3	0.6
α-methylstyrene		No	Reaction
β-methylstyrene		No	Reaction
3-phenylpropylene		No	Reaction

a) Turnover number = [product]/[complex].
Minor products (less than 1%) are; b) 1,2-epoxide,
c) cyclopentanecarboxyaldehyde, and d) norborneol.

solution was stirred vigorously in a closed teflon vial (5 mL) at 50 °C under O_2. The products were analyzed with gas chromatography.

The results of the reactions are shown in Table 1. Linear terminal olefins are oxidized to methyl ketones with 99% selectivity, whereas cyclic olefins are oxidized exclusively to epoxides. Olefins with bulky substituents such as phenyl and benzyl groups are not oxidized.

Compound 1 disproportionates to Pt(II) and Pt(III) dimers on dissolution as follows.[15)]

$$[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+} + L + L' \rightleftharpoons [Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+} + [Pt_2(NH_3)_4(C_4H_6NO)_2LL']^{4+} \quad (1)$$

(L and L′ are axial ligands)

Therefore, the Pt(II) dimer or Pt(III) dimer is conceivably the true catalyst. The catalytic activities of these two species were compared by using electrolytically prepared Pt(II) and Pt(III) dimer solutions,[16)] and the Pt(II) dimer was found inactive, whereas the Pt(III) dimer showed the same activity as **1**. Therefore, the Pt(III) dimer seems to be the real catalyst in the reaction. Olefin coordinates to the Pt(III) dimer in the reaction, which was shown in the UV-vis absorption spectrum. The absorbance of **1** at 480 nm decreases on stepwise addition of 0.5 ml each of 1-octene to 2.5 ml of 0.1 mM CH_2ClCH_2Cl solution of **1**, and a new absorption of the olefin-coordinated Pt(III) dimer at 265 nm increases concomitantly with the isosbestic point at 315 nm. Complex **1** and the Pt(III) dimer are not decomposed after the catalytic reaction ceases, but are reduced to the Pt(II) dimer. This was confirmed by the fact that, after the cease of the reaction, addition of $(NH_4)_2S_2O_8$ recovered both the olefin oxidation reaction and the absorption band of **1** at 480 nm, which had disappeared after the reaction ceases.

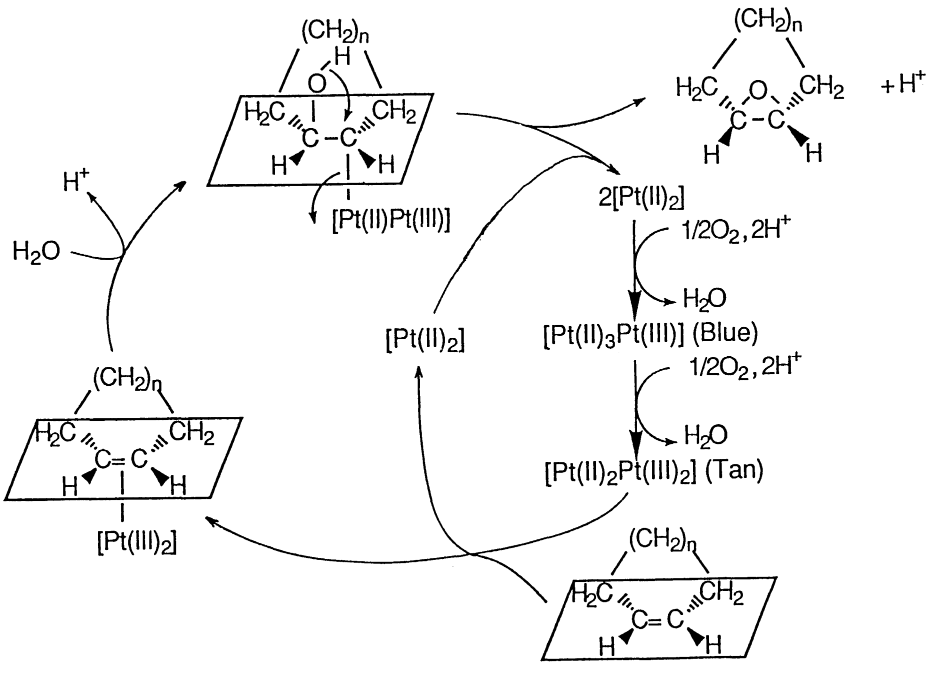


Fig. 1. Possible mechanism for the epoxidation reaction.

The origin of the oxygen atom in the reaction products (ketones and epoxides) was confirmed to be water, by comparing the reaction in

$H_2{}^{16}O$ and 99.5% $H_2{}^{18}O$, and analyzing the products by GC-MS. From these facts, the mechanism seems basically to be similar to the Wacker type process$^{6)}$ as shown in Fig. 1 for the epoxidation. The olefin oxidation takes place only in stoichiometric amount under N_2, and O_2 is necessary to regenerate the Pt(III) dimer. This fact also supports the mechanism in Fig. 1.

The present reaction is the first epoxidation of olefins by water oxygen, with or without any catalyst. The detail of the mechanism is still under investigation.

References

1) B. Meunier, Chem. Rev., 92, 1411(1992).
2) K. A. Jorgensen, Chem. Rev., 89, 431(1987).
3) D. Mansuy, Pure Appl. Chem., 59, 759(1987)
4) H. Mimoun, Angew. Chem., Int. Ed. Engl., 21, 734(1982).
5) R. Holm, Chem. Rev., 87, 1401(1987).
6) J. Tsuji, Synthesis, 369(1984).
7) G. Strukul and R. A. Michelin, J. Am. Chem. Soc., 107, 7563(1985).
8) G. Strukul, R. Sinigalia, A. Zanardo, F. Pinna, and R. A. Michelin, Inorg. Chem., 28, 554(1989).
9) A. Zanardo, R. A. Michelin, F. Pinna, and G. Strukul, Inorg. Chem., 28, 1648(1989).
10) J. K. Barton, C. Caravana, and S. J. Lippard, J. Am. Chem. Soc., 101, 7269(1979).
11) K. Matsumoto and K. Fuwa, J. Am. Chem. Soc., 104, 897(1982).
12) K. Matsumoto, H. Takahashi, and K. Fuwa, Inorg. Chem., 22, 4086(1983).
13) T. Abe, H. Moriyama, and K. Matsumoto, Inorg. Chem., 30, 4198(1991).
14) The compound was prepared by follwing the procedure for **1**. Single crystal X-ray analysis has confirmed the tetranuclear platinum blue structure. The result will be reported separately. Anal Found: C, 14.55; H, 3.95; N, 14.29%. Calcd for $C_{20}H_{64}N_{17}O_{19}Pt_4$: C, 14.76; H, 3.96; N, 14.63%.
15) K. Sakai and K. Matsumoto, Inorg. Chim. Acta, 213, 11,(1993).
16) Electrolyses were carried out at 0.2 V and 0.8 V vs. SCE for Pt(II) and Pt(III) dimers, respectively, in 0.05 M H_2SO_4.

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