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OXIDATIVE ADDITION OF ORGANIC ACIDS TO DIOXYGEN COMPLEXES AND FORMATION OF HYDROGEN PEROXIDE

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Oxidative addition reactions of organic acids to dioxygen complexes are investigated. In the case of $Pt(PPh_3)_2O_2$, hydrogen peroxide is obtained in as much as 70% yield with a platinum carboxylato complex, $Pt(PPh_3)_2(OCOCH_2Cl)_2$. The effect of pKa of the substrates on the oxidative addition of the dioxygen complexes is also examined.

Although the coordinated dioxygen to a metal complex is reported to be peroxidic on the basis of increased O-O bond length,[1,2)] and Vaska[3)] and Wilke[4)] have briefly mentioned the formation of H_2O_2 upon protonation of $IrCl(CO)(PPh_3)_2O_2$ and $Ni(PPh_3)_2O_2$ (PPh_3=triphenylphosphine), respectively, the determination of reaction products and the elucidation of protonation mechanism still remain unclarified. We wish to report that the oxidative addition of organic acids to dioxygen complexes results in the selective formation of H_2O_2 and a platinum carboxylato complex.

All the dioxygen complexes used were prepared according to the literatures.[5)] The reactions were carried out in CH_2Cl_2 solution of CH_3COOH(4.37M.) or $CH_2ClCOOH$(1.00M.) at 0°C. H_2O_2 formed during the reactions was transferred under vacuum prior to iodometric titration, which was employed to raise the precision of the iodometry.

As shown in Table 1, both CH_3COOH and $CH_2ClCOOH$ react with $Pt(PPh_3)_2O_2$ and $Pd(PPh_3)_2O_2$ under air or nitrogen to give H_2O_2 in 52-70% yield(based on the dioxygen complexes used). The formation of H_2O_2 in high yield under N_2 atmosphere strongly suggests that the peroxide titrated is derived from the coordinated oxygen molecule of $M(PPh_3)_2O_2$. In the case of $IrCl(CO)(PPh_3)_2O_2$ or $Ru(OH)(NO)(PPh_3)_2O_2$, the formation of H_2O_2 could scarcely recognized.

Table 1. The formation of H_2O_2 by oxidative addition of organic acids to dioxygen complexes in CH_2Cl_2 at 0°C

Run	Dioxygen complex	x10^5mole.	Acid[a]	Atmosphere	H_2O_2(x10^5mole.)[b]	Yield(%)
2	$Pt(PPh_3)_2O_2$	1.69	CH_3COOH	Air	1.18	70.9
3	$Pt(PPh_3)_2O_2$	1.69	CH_3COOH	N_2	1.30	76.9
6	$Pt(PPh_3)_2O_2$	8.40	$CH_2ClCOOH$	Air	5.58	66.4
7	$IrCl(CO)(PPh_3)_2O_2$	3.71	$CH_2ClCOOH$	Air	trace	-
8	$Ru(OH)(NO)(PPh_3)_2(CO)$	4.48	$CH_2ClCOOH$	O_2	0.18	3.65
9	$Ru(OH)(NO)(PPh_3)_2O_2$	4.44	$CH_2ClCOOH$	Air	0.10	2.16
11	$Pt(PPh_3)_2O_2$	5.74	$CH_2ClCOOH$	Air	3.01	52.4
12	$Pt(PPh_3)_2O_2$	5.74	$CH_2ClCOOH$	Air	0.99[c]	17.2
19	$Pd(PPh_3)_2O_2$[d]	11.28	CH_3COOH	N_2	7.57	67.1
20	$Pd(PPh_3)_2O_2$[d]	11.12	$CH_2ClCOOH$	N_2	8.37	75.3
21	$Pd(PPh_3)_2O_2$[d]	17.66	$CH_2ClCOOH$	N_2	13.11	74.2

a Total volumes are 4 ml. for CH_3COOH(1:1 by volume) and 2 ml. for $CH_2ClCOOH$. Concentrations of CH_3COOH and $CH_2ClCOOH$ are 4.37 and 1.00 M., respectively.
b Titrated by iodometry after 1 hr. c Treated with catalase prior to titration. d Reaction temperature is 2°C.

Analytical data for the colorless metal complex, which is obtained in the reaction of $Pt(PPh_3)_2O_2$ with $CH_2ClCOOH$ and recrystallized from ethanol, are given in Table 2. The complex exhibits intense i.r. absorption at 1604 and 1098cm^{-1} characteristic of platinum-carboxylate and coordinated triphenylphosphine, respectively. Elemental analysis and n.m.r. data also indicate that the structural formula of the complex can be determined to be $Pt(PPh_3)_2(OCOCH_2Cl)_2$. Although the reaction of the platinum dioxygen complex with CH_3COOH was examined in a similar manner, the isolation of the acetate complex from the reaction residue was unsuccessful. However, it was confirmed that i.r. spectrum of the residue had characteristic stretching bands at 1565 and 1098cm^{-1}. The yellow carboxylato complex which is obtained in

Table 2. Analytical data of $Pt(PPh_3)_2(OCOCH_2Cl)_2$

Elemental analysis		C(%)	H(%)	Cl(%)
Found	:	52.40	4.02	7.86
Calcd. for $C_{40}H_{34}Cl_2O_4P_2Pt$	:	52.48	3.72	7.76

M.p. : 252-4°C (decomposition)

I.r. $(CH_2Cl_2)^a$: $1604 cm^{-1}$(C=O), $1098 cm^{-1}$($P-Ph_3$)

^1H n.m.r. $(CDCl_3)^b$: 7.26(30H,m,Ar-H), 3.23(4H,s,CH_2Cl)

a The i.r. spectrum was calibrated with polystyrene film.

b The n.m.r. spectrum was measured at 60 MHz. Chemical shifts are given in ppm relative to TMS on the δ scale. s singlet m multiplet.

the reaction of $Pd(PPh_3)_2O_2$ with $CH_2ClCOOH$ similarly exhibits intense i.r. absorption at 1605(C=O) and $1098 cm^{-1}$($P-Ph_3$).

Furthermore, the effect of pKa of the substrates on the yield of H_2O_2 was also investigated. As shown in Table 3, the yield of H_2O_2 can be roughly correlated with pKa value of the substrates. While the yield of H_2O_2 in the presence of benzoic acid(pKa=4.21) is much less than that in CH_3COOH(pKa=4.76). This result seems to

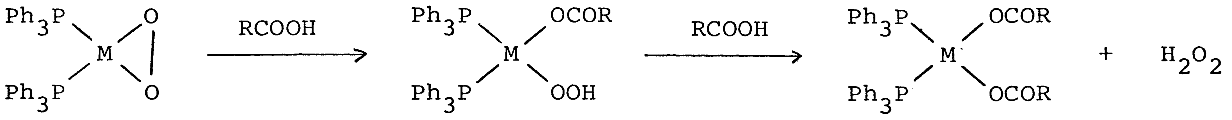
Table 3. The effect of pKa on the oxidative addition of $Pt(PPh_3)_2O_2$ and $Pd(PPh_3)_2O_2$ in CH_2Cl_2 at 0°C[a]

Substrate(1.00M.)	pKa(at 25°C)	H_2O_2(%) $Pt(PPh_3)_2O_2$	H_2O_2(%) $Pd(PPh_3)_2O_2$[b]
Monochloroacetic acid	2.86	66.4	75.3
Benzoic acid	4.21	18.9	32.7
Acetic acid	4.76	76.9[c]	53.5
p-Nitrophenol	7.15	-	7.1
p-Acetylphenol	~8	8.6	-
Phenol	10	-	8.9
Indene	21	-[d]	-[d]

a Reactions were carried out under N_2 for 1 hr. b Reaction temperature was 2°C. c Concentration of CH_3COOH was 4.73M. d No peroxide was detected by iodometry.

suggest that the oxidative addition is influenced by steric factor. Also phenols react with the dioxygen complexes to give H_2O_2 in 7.1-8.9% yield.

From these results, the following mechanism for the oxidative addition can be depicted,



The reaction may proceed by stepwise mechanism through an intermediate in which the H_2O_2 formation and the oxidative addition are concerted processes.

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