Reaction of Carboxylic Acids with Dioxygen Complexes: A Mechanistic Aspect of the Reaction[1]

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The reaction of carboxylic acids with dioxygen complexes $MO_2(PPh_3)_2$(M=Pt, Pd) at low temperature gives rise to the selective formation of H_2O_2 and the corresponding dicarboxylato complexes characterized by their physical properties. It is suggested that the reaction can be influenced by either the capability of reactant for coordination to metal center or the stability of resulting metal complex. An equimolar addition of $CH_2ClCOOH$ to the dioxygen complexes in the presence of triphenylmethyl bromide at *ca.* −70 °C gives triphenylmethyl hydroperoxide and the corresponding monocarboxylato complexes in good yields, indicating that the reaction of organic acids with $MO_2(PPh_3)_2$ proceeds by stepwise mechanism.

Recently a study on the reaction of metal dioxygen complexes with a variety of organic compounds has received considerable attention. In general, the coordinated molecular oxygen to a metal complex is considered to be peroxidic on the basis of increased O–O bond length.[2] Benzoyl chloride and triphenylmethyl bromide (TPMB) react with $NiO_2(t\text{-BuNC})_2$ to give the corresponding peroxides.[3] Although Vaska[4] and Wilke *et al.*[5] also mentioned the formation of H_2O_2 upon protonation of $IrO_2Cl(CO)(PPh_3)_2$ and $NiO_2(PPh_3)_2$, respectively, the determination of reaction products and the elucidation of protonation mechanism still remain unclarified. In order to elucidate the reaction mechanism, the reaction of some carboxylic acids and phenols with square planar dioxygen complexes $MO_2(PPh_3)_2$ (M=Pt, Pd) was investigated.

In this work, we wish to report that the reaction of organic acids with $MO_2(PPh_3)_2$ results in the selective formation of H_2O_2 and the corresponding dicarboxylato complexes, and that the reaction proceeds by stepwise mechanism. The reaction of *o*- and *p*-substituted phenols was investigated in detail.

Experimental

Melting points were determined on a Yazawa hot-stage apparatus and uncorrected. Chloroacetic acid, triphenylphosphine(PPh_3), and TPMB were purified by recrystallization from ethanol or benzene. All the dioxygen complexes were prepared according to the procedure in literature.[6] The IR spectra were recorded as Nujol mulls on a Nippon Bunko IR-G spectrophotometer(4000—400 cm^{-1}), calibrated with polystyrene film. The NMR spectra were obtained on a JEOL Model JMN-4H-100 spectrometer in $CDCl_3$ solution containing tetramethylsilane as an internal standard. H_2O_2 and triphenylmethyl hydroperoxide obtained by equimolar addition of $CH_2ClCOOH$ to the dioxygen complexes in the presence of TPMB were analyzed by the conventional iodometric method.

General Procedure. The reactions were carried out in CH_2Cl_2 solution in the air or under a nitrogen atmosphere at 0 °C. The total volume was 4 ml for CH_3COOH(4.37 M) and 2 ml for $CH_2ClCOOH$(1.00 M). The concentration of $MO_2(PPh_3)_2$ was in the range 4.23×10^{-3}—8.83×10^{-2} M. The peroxide formed during the course of reaction was transferred in a vacuum(*ca.* 10^{-2}Torr) and then titrated by iodometry. The transfer efficiency was *ca.* 98 percent. The peroxide transfered could be considered principally to be H_2O_2 since the amount of the peroxide drastically decreased when treated with catalase.

Preparation of Dicarboxylato Complexes. *$Pt(OCOCH_2Cl)_2(PPh_3)_2$*: To a CH_2Cl_2 solution (20 ml) of $PtO_2(PPh_3)_2 1.5C_6H_6$(0.186 g, 0.214 mmol) was added excess $CH_2ClCOOH$(0.189 g, 2.00 mmol) under N_2 at 0 °C. Immediately the yellow solution turned colorless. The solution was stirred for 1 h at room temperature. Removal of the solvent *in vacuo* left a white residue which was recrystallized from ethanol to yield a white solid(0.134 g, 88.2% based on the dioxygen complex used). The solid was identified as $Pt(OCOCH_2Cl)_2(PPh_3)_2$ on the basis of its physical properties(Table 3).

$Pd(OCOCH_2Cl)_2(PPh_3)_2$: A similar treatment of $PdO_2(PPh_3)_2$(0.183 g, 0.235 mmol) with $CH_2ClCOOH$(0.189 g, 2.00 mmol) afforded a yellow solid of $Pd(OCOCH_2Cl)_2(PPh_3)_2$ (0.127 g, 87.7%) which was recrystallized from hexane–ethanol (1: 1 by volume). Physical properties for the yellow solid are also given in Table 3.

Preparation of Monocarboxylato Complexes. *$Pt(OCOCH_2Cl)Br(PPh_3)_2$*: To a CH_2Cl_2 solution(50 ml) of $PtO_2(PPh_3)_2 1.5C_6H_6$(0.869 g, 1.00 mmol) was added equimolar $CH_2ClCOOH$(0.107 g, 1.13 mmol) under N_2 at the temperature of ethanol–Dry Ice. After the resulting orange solution was stirred for 5 min, TPMB(0.329 g. 1.02 mmol) was slowly added. The reaction mixture was stirred another 3 h at the same temperature. The orange solution was allowed to stand overnight in a refrigerator. The reaction mixture containing an appreciable amount of white precipitated was distilled *in vacuo* at room temperature to give 0.841 g(yield 94.2%) of the monocarboxylate, white solid, along with colorless crystals which were chromatographed on alumina(about 300 mesh, deactivated with 1 ml of H_2O/100 g of alumina) and eluted with diethyl ether. The colorless crystals were identified as triphenylmethyl hydroperoxide from the data of its elemental analysis(Found: C, 82.89, H, 5.81%. Calcd for $C_{19}H_{16}O_2$: C, 82.57; H, 5.81%), mp (83—84 °C, lit,[7] 81—82 °C), IR, and chemical reactions. The hydroperoxide exhibited intense IR absorption at 3490 cm^{-1} characteristic of hydroperoxy moiety which shifted at higher frequency (3540 cm^{-1}) when treated with excess PPh_3, indicating that the peroxide was reduced to the corresponding alcohol. The yield of triphenylmethyl hydroperoxide was 0.230 g (83.5% based on the dioxygen complex used).

$Pd(OCOCH_2Cl)Br(PPh_3)_2$: A similar treatment of $PdO_2(PPh_3)_2$(0.789 g, 1.00 mmol) with TPMB(0.291 g, 0.990 mmol) in the presence of $CH_2ClCOOH$(0.107 g, 1.13 mmol) gave a yellow solid of $Pd(OCOCH_2Cl)Br(PPh_3)_2$(0.582 g, 81.4%) and triphenylmethyl hydroperoxide(0.291 g, 50.6% based on TPMB used) which was also purified by the chromatographic method under the same conditions, using benzene–diethyl ether as an eluent. As a by-product, a similar yellow solid was isolated from the residue insoluble in CH_2Cl_2. The solid was

Table 1. Formation of H_2O_2 by the reaction of organic acids with dioxygen complexes in CH_2Cl_2 at 0 °C

Dioxygen complex	$\times 10^5$ mol	Acid	Atmosphere	H_2O_2[a] ($\times 10^5$ mol)	Yield[b] (%)
$PtO_2(PPh_3)_2$	1.69	CH_3COOH	Air	1.18	70.9
	1.69	$CH_2ClCOOH$	N_2	1.30	76.9
	8.40	$CH_2ClCOOH$	Air	5.58	66.4
	5.74	$CH_2ClCOOH$	N_2	3.01	52.4
	5.74	$CH_2ClCOOH$	N_2	0.99[c]	17.2
$PdO_2(PPh_3)_2$[d]	11.28	CH_3COOH	N_2	7.57	67.1
	11.12	$CH_2ClCOOH$	N_2	8.37	75.3
	17.66	$CH_2ClCOOH$	N_2	13.11	74.2
	7.18	$CH_2ClCOOH$	N_2	5.60	76.6
	7.18	$CH_2ClCOOH$	N_2	0.02[c]	0.24
$IrO_2Cl(CO)(PPh_3)_2$	3.71	$CH_2ClCOOH$	Air	trace	—
$RuO_2(OH)(NO)(PPh_3)_2$	4.44	$CH_2ClCOOH$	Air	0.10	2.16

a) Titrated by iodometry after 1 h. b) The yields were calculated on the basis of the dioxygen complexes used. c) Treated with catalyse prior to titration. d) Reaction temperature was 2 °C.

characterized as $PdBr_2(PPh_3)_2$ by analysis (Found: C, 54.46; H, 3.87; Br, 20.18%. Calcd for $C_{36}H_{30}Br_2P_2Pd$: C, 54.46; H, 3.83; Br, 20.21%). The IR spectrum was identical with that of an authentic sample prepared by other routes.

Results and Discussion

Reaction of Carboxylic Acids with $MO_2(PPh_3)_2$. The experimental results on the reaction of CH_3COOH or $CH_2ClCOOH$ with $MO_2(PPh_3)_2$ (M=Pt, Pd) are given in Table 1. $MO_2(PPh_3)_2$ reacted with the organic acids in the air or under a nitrogen atmosphere to give H_2O_2 in 52—77% yield (based on the dioxygen complexes used). The high yields of H_2O_2 under N_2 strongly indicate that H_2O_2 is derived from the coordinated molecular oxygen of $MO_2(PPh_3)_2$. The fact that the yields of H_2O_2 under air are less than those under N_2 suggests that the reaction proceeds stoichiometrically. Formation of H_2O_2 was scarcely recognized in the reaction of $IrO_2Cl(CO)(PPh_3)_2$ and $RuO_2(OH)(NO)(PPh_3)_2$ with $CH_2ClCOOH$.

Table 2. Effect of pK_a on the yields of H_2O_2 at 0 °C[a]

Acid (1.00 M)	pK_a (at 25 °C)	H_2O_2 Yield (%) $PtO_2(PPh_3)_2$	H_2O_2 Yield (%) $PdO_2(PPh_3)_2$[b]
Chloroacetic 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	9.99		8.9
Hydroquinone[d]	9.91[e]	5.3	
Catechol[d]	9.45	85.1	33.6
Catechol[d]	9.45	1.2[f]	trace
3,5-Di-*t*-butyl-catechol[d]	≈9	66.5	32.0
o-Aminophenol[d]		83.2	36.5
Indene	21	—[g]	—[g]

a) All the reactions were carried out under N_2 for 1 h. b) Reaction temperature was 2 °C. c) [CH_3COOH] was 4.73 M. d) Concentration of phenols was 8.25×10^{-2} M. e) pK_a value at 20 °C. f) Treated with catalase prior to iodometry. g) No peroxide was detected by iodometry.

The effect of $pK_a(H^+)$ of the organic acids on the yield of H_2O_2 was also investigated. The yield of H_2O_2 seems to be roughly correlated with the pK_a of substrates (Table 2). Namely the formation of H_2O_2 shows an upward trend with the decreased pK_a value. However, the yield in the presence of bonzoic acid (pK_a= 4.21) was much less than that in CH_3COOH (pK_a= 4.76). *o*-Substituted phenols reacted with **1a** under the same conditions to provide H_2O_2 in 83—85% yield, suggesting that the reaction is fairly influenced by either the capability of substrates for coordination to the metal center or the stability of the resulting metal complex. Namely, the reason why *o*-substituted phenols are more preferred is that their dianions are good ligands. From these results, the following reaction seems to take place.

$$\underset{\textbf{1a};\ M=Pt}{\underset{\textbf{1b};\ M=Pd}{MO_2(PPh_3)_2}} + 2RCOOH \longrightarrow M(OCOR)_2(PPh_3)_2 + H_2O_2 \quad (1)$$

3a; M=Pt, R=CH_2Cl
3b; M=Pd, R=CH_2Cl
3c; M=Pt, R=CH_3
3d; M=Pt, R=C_6H_5

The analytical data for dicarboxylato complexes **3a** and **3b** obtained in the reaction of $MO_2(PPh_3)_2$ with $CH_2ClCOOH$ and recrystallized from ethanol are given in Table 3. The infrared spectra of **3a** and **3b** are similar to each other. Whereas **1a** and **1b** showed intense absorption due to oxygen-oxygen stretching, respectively, at 821 and 869 cm^{-1}, there were no strong bands in the 900—800 cm^{-1} region for the carboxylates. No band was observed in the region of the spectra near 2200 cm^{-1} which can be attributed to a metal-hydrogen stretching.[8] The complexes exhibited absorptions at 1644—1624 and 1099 cm^{-1} characteristic of a metal-carboxylate and coordinated PPh_3, respectively. The large shift of the ν(C=O) bands of **3a** and **3b** to lower frequency from that of the corresponding free acid

Table 3. Analytical data of the carboxylates

Complex	Mp (°C)	Formula	Analysis (%) Calcd (Found) C	H	Cl	Br	IR(in CH_2Cl_2), cm^{-1}
3a	252—254(dec)	$C_{40}H_{34}O_4Cl_2P_2Pt$	52.48 (52.40)	3.72 (4.02)	7.76 (7.86)		1624m, 1604m, and 1099s
3b	152—157(dec)	$C_{40}H_{34}O_4Cl_2P_2Pd$	58.73 (58.02)	4.16 (4.87)	8.69 (8.65)		1644s, 1608m, and 1099s
4a[a)]	267—269(dec)	$C_{41}H_{38}O_2BrClP_2Pt$	52.81 (52.72)	3.79 (3.83)	3.81 (3.69)	8.57 (8.83)	1662s, 1603w, 1607sh, and 1097s
4b[a)]	145—154(dec)	$C_{41}H_{38}O_2BrClP_2Pd$	58.38 (58.19)	4.19 (4.40)	4.21 (3.92)	9.47 (11.01)	1660sh, 1646w, 1606s, and 1098s

a) Calcd as $M(OCOCH_2Cl)Br(PPh_3)_2 \cdot 0.5C_6H_6$. w; weak, m; medium, s; strong, sh; shoulder.

seems to be due to the interaction between the carbonyl moiety and the central metal. These dicarboxylato complexes gave elemental analyses (Table 3) consistent with the proposed structures, respectively. The NMR spectra also indicates that the complexes could be characterized as $M(OCOCH_2Cl)_2(PPh_3)_2$. Similarly it was confirmed that **3c** and **3d** had characteristic absorptions at 1565 and 1617 cm^{-1}, respectively, attributable to the ν(C=O) of coordinated carboxylates.

Mechanistic Aspect of the Reaction. When **1a** and **1b** were treated with double molar quantity of $CH_2ClCOOH$ at *ca.* −70 °C, characteristic color changes of the solution were observed. The CH_2Cl_2 solution of **1a** gradually turned orange from yellow and then became colorless. In a similar manner, **1b** changed from light blue to wine red, and then to yellow. The IR spectra of **1a** and **1b** treated with exactly equimolar $CH_2ClCOOH$ to the complexes at *ca.* −70 °C were taken in CH_2Cl_2 solution at ambient temperature. Although the spectra were very similar to those of the corresponding dicarboxylates, an other new strong band was observed at *ca.* 3380 cm^{-1} which might be attributed to an oxygen-hydrogen stretching. No band due to the ν(C=O) of free acid was, of course, observed in the region of the spectra near 1700 cm^{-1}. Treatment of **1a** with CH_3COOD under the same conditions also gave an IR spectrum having the characteristic new band at *ca.* 2500 cm^{-1} which might be assigned to the ν(O–D). The results suggest that the reaction of $CH_2ClCOOH$ with $MO_2(PPh_3)_2$ proceeds by stepwise mechanism as shown below:

$$MO_2(PPh_3)_2 \xrightarrow{CH_2ClCOOH} M(OOH)(OCOCH_2Cl)(PPh_3)_2$$
2a; M=Pt
2b; M=Pd

$$\xrightarrow{CH_2ClCOOH} M(OCOCH_2Cl)_2(PPh_3)_2 + H_2O_2 \quad (2)$$
3a; M=Pt
3b; M=Pd

The reaction of a metal hydride with gaseous oxygen gives a metal hydroperoxide as a reactive intermediate.[9] In our complexes, isolation of **2a** and **2b** from the reaction mixtures was unsuccessful because of their thermal labilities. **2b** in particular was unstable in solution and decomposed to give palladium metal when allowed to stand for several minutes at room temperature. In order to elucidate the reaction mechanism, we attempt to prepare triphenylmethyl hydroperoxide by the successive equimolar addition of $CH_2ClCOOH$ and TPMB to $MO_2(PPh_3)_2$ at −70 °C as shown in the following.

$$MO_2(PPh_3)_2 \xrightarrow[\text{in } CH_2Cl_2]{CH_2ClCOOH} M(OOH)(OCOCH_2Cl)(PPh_3)_2$$
$$\xrightarrow{TPMB} M(OCOCH_2Cl)Br(PPh_3)_2 + Ph_3COOH \quad (3)$$

In the reaction of **1a** and **1b**, the hydroperoxide was obtained in 83.5 and 50.7% yields, respectively. In the absence of the complexes no peroxidation of TPMB with gaseous oxygen took place at all. The lower yield in **1b** seems to be due to a smaller stability of **2b**.

Analytical data for the monocarboxylates are given in Table 3. The IR spectra of **4a** and **4b** were close to those of the corresponding dicarboxylates. The NMR spectra of **4a** and **4b**, taken in $CDCl_3$ solution, exhibited singlet peaks at δ 3.31 and 3.39 ppm, respectively, which were easily assignable to their methylene protons. The identification of hydroperoxide was performed by its physical properties and chemical reactions (see Experimental).

The results strongly suggest that the reaction of $MO_2(PPh_3)_2$ with carboxylic acids proceeds by stepwise mechanism (2).

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