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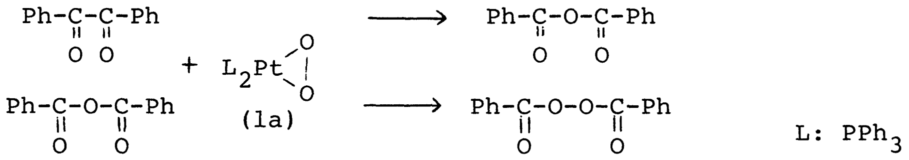
OXYGEN ATOM TRANSFER REACTION
THE REACTION OF CARBONYL COMPOUNDS WITH DIOXYGEN COMPLEXES

Shun'ichi AIDA, Hiroyuki OHTA*, and Yoshio KAMIYA
Department of Reaction Chemistry, Faculty of Engineering,
University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113

The reaction of peroxobis(triphenylphosphine)platinum with benzil or benzoic anhydride gave benzoic anhydride or benzoyl peroxide respectively. The scope of the above reactions is described.

Oxygen atom transfer reaction is one of the current interests and many papers have been published from two aspects.[1-8] The first is concerned with the model reactions for monooxygenase catalysed oxygen atom transfer,[1-6] and the second is its synthetic utility to produce epoxide or ketones.[7-8] The reported "oxenoid reagent" like iodosobenzene[4] and pyridine-N-oxide[5] can transfer an oxygen atom to alkanes, alkenes, and sulfides.

During our research on the nucleophilic reactivity of coordinated dioxygen of the dioxygen metal complex,[9] we have found that peroxobis(triphenylphosphine) platinum(II)(1a) reacts as an oxygen atom transfer reagent toward certain carbonyl compounds.[10] The following general equations present our results.



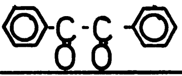
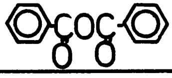
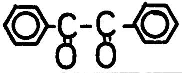
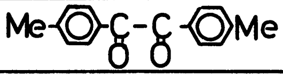
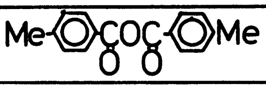
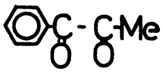
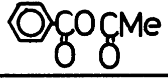
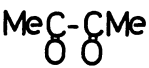
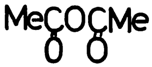
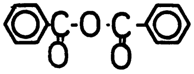
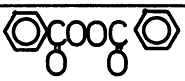
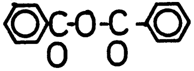
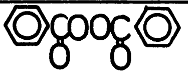
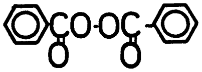
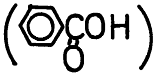
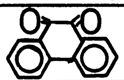
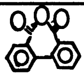
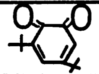
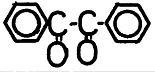
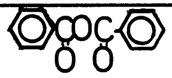
$$\text{Ph-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-Ph} + L_2Pt\langle^{O}_{O}| \;(1a) \longrightarrow \text{Ph-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-O-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-Ph}$$

$$\text{Ph-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-O-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-Ph} + L_2Pt\langle^{O}_{O}| \;(1a) \longrightarrow \text{Ph-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-O-O-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-Ph}$$

L: PPh_3

In general, the experiment was performed by mixing equimolar amounts of the complex and a substrate (0.1 mmol) in 1 ml of methylene chloride under argon or dry air in a sealed vial. Both yield and distribution of the products do not depend on the atmosphere. The results are summarized in the table.

Table

Run	Substrate	Complex	Reaction time	Conversion	Oxygen transferred product	Yield[d]
1		1a[a]	28 h	74 %		55 %
2		1b[b]	30	0	–	–
3		1a	190	83		14
4		1a	3	91		30
5	 $\mathrm{Me\underset{O}{C}\text{-}\underset{O}{C}Me}$	1a	90	10	 $\mathrm{Me\underset{O}{C}O\underset{O}{C}Me}$	0
6		1a	2	95		9
7		1b	20	0		0
8		1a	2	58		52
9		1a	10	42		41
10		1a	<1	100		0
11		1c[c]	30	0		0

a: $PtO_2(PPh_3)_2$ b: $PdO_2(PPh_3)_2$ c: Co(Salpr),O_2 d: Based on the consumed substrate determined by GC. e: Isolated yield

Run 1,2 and 6,7 reveal a remarkable difference in reactivity between palladium and platinum complex, that palladium complex is inactive toward the substrates employed. An edge on type dioxygen complex such as Co(Salpr)---O_2 did not afford benzoic anhydride or benzoic acid on treatment with benzil (run 11).[11]

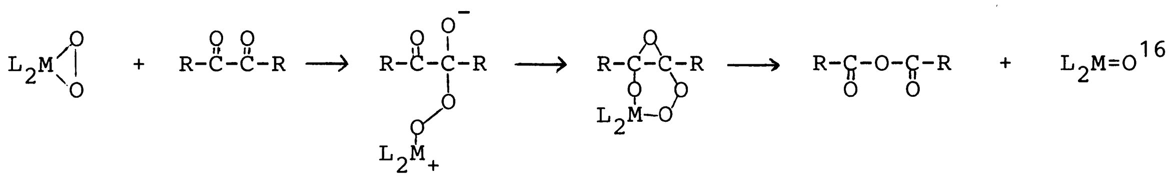
Run 1-5 shows that the reactivity of the substrate considerably depends on its structure. Thus, benzil reacts six times faster than p',p'-dimethyl benzil, while biacetyl reacts very slowly and the formation of acetic anhydride or acetic acid was not detected by gas chromatography. The different behavior of biacetyl from that of benzil is probably attributable to the fact that methyl group is more electron donating than phenyl group, and methyl substitution will retard the nucleophilic susceptibility by the coordinated dioxygen.

Interestingly, benzoic anhydride reacts with (1a) to afford dibenzoyl peroxide (run 6). This result recalls an analogous reaction that potassium superoxide (KO_2) reacts with acid anhydride to yield diacyl peroxide.[12]

When dibenzoyl peroxide was treated with (1a), benzoic acid was produced as a main product. A recent report of singlet oxygen generation from potassium superoxide and diacyl peroxide evokes fresh concern,[13] since similar reaction may also be expected for the bound dioxygen. In our case, however, formation of singlet oxygen is unlikely, because the reaction carried out in the presence of 9,10-diphenylanthracene, a singlet oxygen quencher,[14] did not afford its endoperoxide.

Run 9 and 10 indicate that cyclic α-diketones react with (1a), but the yield of oxygen atom transferred product strongly depends on the substrate. Especially, when 3,5-di-tert-butyl-o-quinone was employed, it disappeared rapidly and the precipitate was formed instantly, but no oxygen atom transferred product was detected in the reaction mixture. Precipitation is indicative of new complex formation.

For the mechanism of the present oxygen atom transfer reactions, the following Baeyer-Villiger scheme would be plausible, considering the nucleophilic reactivity of the bound dioxygen molecule.[15]



L; PPh_3, M: Pt

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16. We were unable to isolate such a metal oxo complex due to complexity of the reaction products.

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