The Reactions of Aroyl Peroxides with Grignard Reagents. III. On the Structure and the Reaction of the Complex Containing Benzoyl Peroxide[1]

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The orange-colored complex which is formed in the reaction of benzoyl peroxide with Grignard reagent was studied by infrared spectra, and the reaction of the complex with Grignard reagent was also examined. In this complex, the structure of BPO was still maintained by coordinating with magnesium atom through the peroxidic as well as the carbonyl oxygen atoms. Reaction products of this complex with phenylmagnesium bromide were benzoic acid(as Mg-salts), phenyl benzoate, benzophenone, triphenylcarbionol, and bromobenzene. The heterolytic mechanism on the formation of bromobenzene was proposed. The molar ratio of products depended seriously upon the mode of addition of Grignard reagents. The exclusive formation of bromobenzene and Mg-salts of benzoic acid without phenyl benzoate under an experimental condition was explained by assuming the electron-transfer process through the coordinating bond in the complex.

The two complexes were isolated in the reaction of benzoyl peroxide (BPO) with Grignard reagents, and analytical data of their components were reported previously.[2] The mechanism of the first stage of this reaction has been proposed on the basis of the relative reactivities of several peroxides.[3] In this paper, the detailed studies on the second stage of the reaction, which was found to proceed more slowly than the first stage,[3] will be reported.

Results and Discussion

Structure of the Complex II. The white complex, which has been named as the Complex I, is produced when the molar ratio [PhMgBr]:[BPO] is 1.33: 1.0, and this was found to be the same structure with the carbonated PhMgBr. Another orange-colored complex, which is named as the Complex II, is obtained when the molar ratio is 0.66:1.0,[3] and this is obtained also by mixing 2 mol of the Complex I with 1 mol of BPO.[2] In order to confirm the previous and tentatively proposed formulae for these complexes, they were submitted to infrared spectroscopy. The tetrahydrofuran (THF) solutions of the Complex I and II have very similar absorption bands with one another as shown in Figs. 1 and 2. The solution of BPO shows a quite different spectrum, which has three intense absorption bands at 1792, 1770, and 1214 cm^{-1} (Fig. 3). If these data were solely taken into consideration, one may arrive at an erroneous conclusion that the peroxide linkage, which had been proposed to be maintained in the Complex II, has already been broken. However, the Complex II produces phenyl benzoate if it is allowed to react with PhMgBr. Considering that phenyl benzoate is the primary product of the reaction of BPO with PhMgBr and that PhCOOMgBr reacting with PhMgBr does produce benzophenone, benzoyl peroxide is concluded to be alive in the Complex II.

The IR spectra of the Complex I and II have two main absorption bands at 1640 and 1415 cm^{-1}, both of which are poorly resolved triplets. The Complex I, reacts with PhMgBr to produce benzophenone and triphenylcarbinol in the similar manner to phenyl benzoate, though the reaction is remarkably slow. This fact means that the grouping –CO–O–MgBr in the Complex I has substantially an ester character. Thus, the absorption band at 1640 cm^{-1} can be assigned mainly to the C=O stretching vibration, which

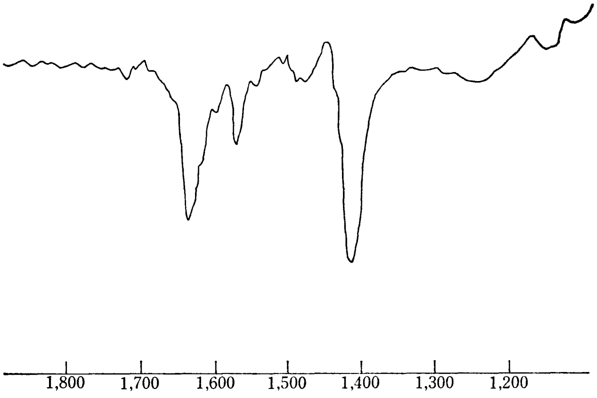

Fig. 1. IR spectrum of the complex I in THF. (cm^{-1})

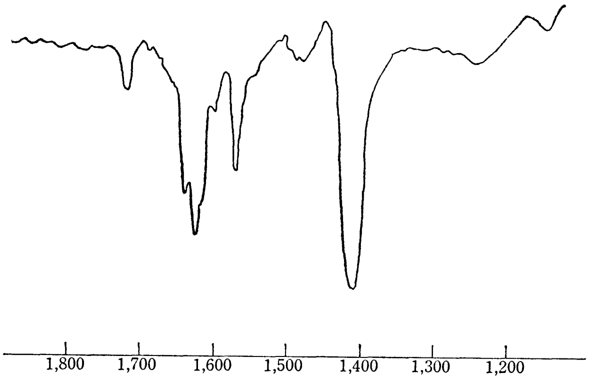

Fig. 2. IR spectrum of the complex II in THF. (cm^{-1})

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[1] The main part of this work was done at Department of Chemistry, Faculty of Science, Kyoto University.

[2] M. Ōkubo, K. Maruyama, and J. Ōsugi, This Bulletin, **42**, 1162 (1969).

[3] M. Ōkubo, K. Marayama, and J. Ōsugi, *ibid.*, in press.

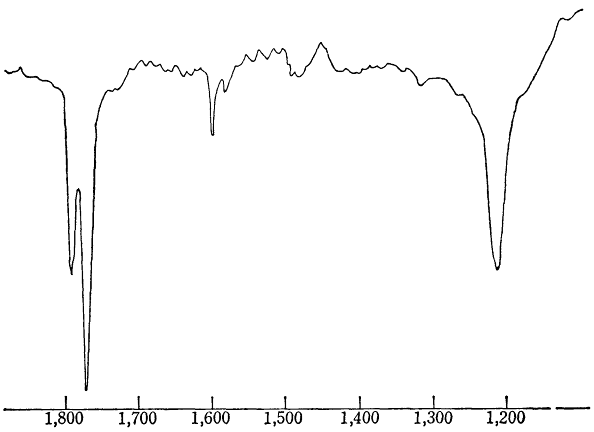


Fig. 3. IR spectrum of BPO in THF. (cm^{-1})

appears at 1770 and 1792 cm^{-1} in the case of free BPO(the difference is about -140 cm^{-1}). The other band at 1415 cm^{-1} can be assigned mainly to the C–O stretching vibration, which appears at 1214 cm^{-1} in the case of free BPO(the difference is about $+200$ cm^{-1}). These shifts(-140 and $+200$ cm^{-1}) are considered to correspond to reasonable changes of bonding energies which are about -0.4 and $+0.6$ kcal/mol. Taking account of analytical data of the Complex I[1] and of the fact that the coordination number of magnesium can be varied between four and six, the Complex I would exist as dimeric state which is depicted in Fig. 4.

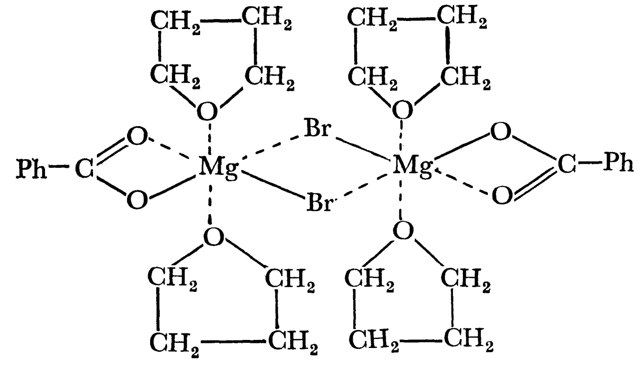


Fig. 4. Structure of the complex I.

Benzoyl peroxide in the Complex II, which shows the quite similar IR spectrum to that of the Complex I, must have almost the same structure as the PhCOO-grouping in the Complex I. Taking account of analytical data of the Complex II[2] and of the coordination number of magnesium, the structure of the Complex II may be depicted as Fig. 5.

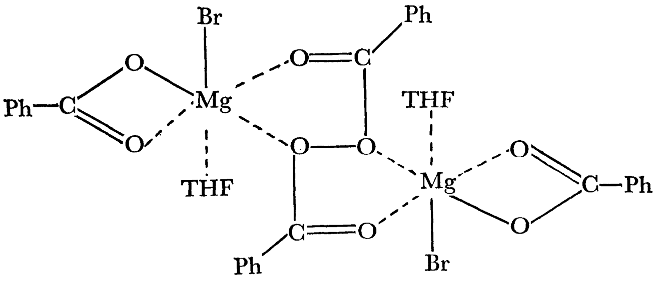


Fig. 5. Structure of the complex II.

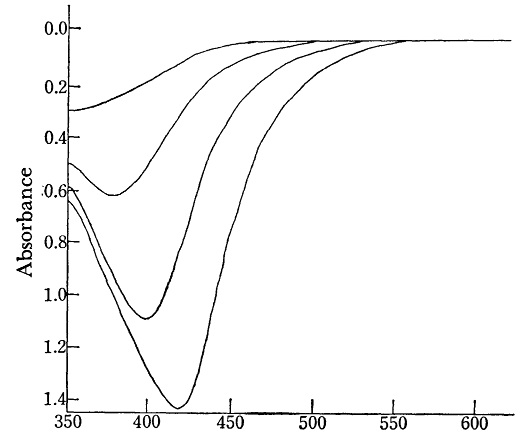


Fig. 6. Visible absorption spectra of the complex II in THF concentration; 10^{-4}—10^{-5} mol/*l*.

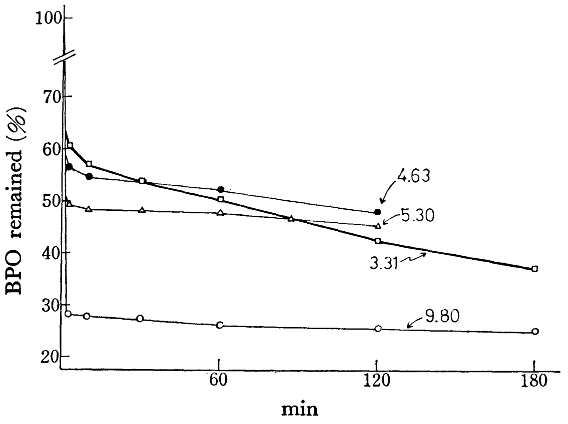


Fig. 7. Effect of concentration on the decomposition of BPO.
Molar ratio [PhMgBr]:[BPO]$=1:1$
Numbers in the Fig. : Molar concn. $\times 10^3$ mol/*l*

The visible absorption spectra of Complex II in THF was found to be dependent on the concentration as shown in Fig. 6. As the concentration is higher, the absorption maximum is shifted to longer wavelengths. This fact may be explained by considering the change of the degree of aggregation of this complex with the change of concentration. This suggestion is borne out by the examination of the effect of the concentration on the rate of the decomposition of BPO with PhMgBr when the molar ratio is 1:1 (Fig. 7). The second stage of the reaction is remarkably slow,[3] and the main reaction of this stage is apparently concerned with the reaction of the Complex II with remaining PhMgBr. It is noted that the curve for the second stage in Fig. 7 becomes steeper as the concentration of the initial reactants is lower though the crease of the curve falls down as the concentration is higher. This fact may be the result that the lower aggregates which might exist in diluted solutions react faster with the remaining Grignard reagent. Thus, the Complex II is considered to exist as aggregated state in the more concentrated solution.

Reaction of the Complex II For the purpose of clarification of the second stage of the reaction, the reaction of the Complex II with PhMgBr must be

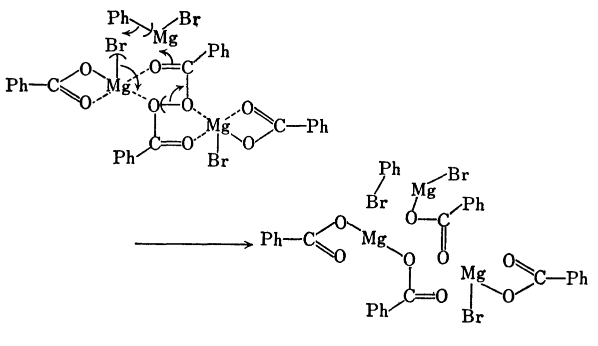
TABLE 1. REACTIONS OF THE COMPLEX II WITH PhMgBr

Expt. No.	Molar ratio[a] $\frac{[PhMgBr]}{[Complex II]}$	Time for addn. hr	Yields[c] %					
			PhBr	PhH	PhCOOH	PhCOOPh	PhCOPh	Ph_3COH
1	2	0	26.6	—	135	36.6	17.8	10.3
2	1 + 1[b]	0[b]	28.5	—	142	36.0	17.0	11.5
3	2	2.5	30.9	—	184	small amount	trace	non
4	2	4.0	31.5	found	192	non	non	—
5	1.5	2.5	39.0[d]	found	187	non	non	non

a) 0.00570 mol of PhMgBr in 30 ml of THF (0.19M) was added to 0.00285 mol of the Complex in 50 ml of THF.
b) 0.00570 mol of PhMgBr in 30 ml of THF was divided into two portions. The first portion was added at once, and the second portion was also added at once after 2 hr.
c) Yields were calculated based on PhMgBr used ([PhMgBr]/[Complex II]=2).
d) The yield is calculated bassd on PhMgBr used ([PhMgBr]/[Complex II]=1.5).

examined.[4] If the twice moles of Grignard reagent were added at once to the THF solution of the Complex II at 0°C, the orange color of the solution disappeared immediately and the peroxide was found to be consumed almost completely. Bromobenzene (26.6%), phenyl benzoate (36.0%), benzophenone (17.8%), and triphenylcarbinol (10.3%) were obtained from the neutral part. The latter three products obviously come from the reaction of PhMgBr with BPO in the Complex II. The formation of the appreciable amount of bromobenzene must be the result of the attack on the Mg-Br linkage in the Complex II by the phenyl group of the Grignard reagent. The question, whether the Mg–Br bond in the complex is broken heterolytitcally or homolytically, is then to be solved.

The molar ratio of the products was found to be affected remarkably by the mode of addition of PhMgBr solution. The results were summarized in Table 1. In the experiment No. 1, two molar equivalents of PhMgBr were added at once to BPO solution. In No. 2, a first equivalent of PhMgBr is added to BPO solution at once and the second equivalent was also added at once after 2 hr. In No. 3, two molar equivalents were added dropwise as slow as the orange color of the solution did not fade during the addition, using an ordinary dropping funnel. In No. 4 and No. 5, 2 and 1.5 equivalents were added in very small drops by using a burette, respectively, and slowly in the similar manner to No. 3. It is to be noted that the amounts of bromobenzene and benzoic acid gradually increased and those of phenyl benzoate, benzophenone and triphenylcarbinol decreased remarkably as the rate of addition is slowed down and as the size of a drop of PhMgBr solution becomes small. This result can be interpreted by the following discussion. The localized high PhMgBr concentration which may appear in the reaction systems of No. 1 and No. 2, will cause a number of Grignard molecules to make attack on the several sites of the Complex II. Thus, bromobenzene is formed if the Mg–Br bond is attacked, and phenyl benzoate is formed if BPO is attacked when it is dissociated as the Complex II is decomposed. On the other hand, if PhMgBr is added slowly and in very small drops, the Mg–Br bond is attacked exclusively as the result of the electron-transfer process which leads to the selective formation of bromobenzene and magnesium salts of benzoic acid probably according to the following mechanism: This electron-transfer process must be fairly slow though the most reactive site of the Complex II is the one of the Mg–Br bonds, since the exclusive formation of bromobenzene and benzoic acid salts is effected only if the Grignard reagent is added very slowly. It is shown in Table 1 that the slow addition causes the yield of benzoic acid to approach 200%, and this fact is also explained by the above mechanism.



The recovery of the phenyl group of PhMgBr is about 100% in the experiments No. 1 and No.2(50% based on PhMgBr), and as low as about 30—39% in the experiments No. 3, No. 4, and No. 5. As benzene was detected in No. 4 and No. 5, the Complex I which is reproduced in the reaction may coordinate to the unreacted PhMgBr and may stabilize this.[5] However, the important fact is that the yield of bromobenzene increases as the rate of addition is slowed down but does not exceed 50% based on the Complex II.[6] This

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4) The solution of the Complex II was prepared by adding a half equivalent of BPO to a completely carbonated PhMgBr solution.[2] See experimental section.

5) The coordination of PhMgBr to PhCOOMgBr is reasonable, since the Complex I can react with PhMgBr at higher temperatures to produce benzophenone and finally triphenylcarbinol. But this reaction is very slow at 0°C as stated in the preceding section.

6) In No. 4, the orange color of the reaction mixture disappeared before the total volume of the PhMgBr solution was added. In No. 5, the orange color of the Complex II was just found to disappear when 1.5 molar equivalents of PhMgBr solution were added. On this base, the yield of bromobenzene is 49%. Since two molar equivalents of the Complex I are reproduced from one molar equivalent of the Complex II according to the above-proposed mechanism, one molar equivalent of PhMgBr is consumed to produce bromobenzene, and the remaining molar equivalent may be coordinated by the reproduced Complex I at 0°C.

may be illustrated by considering that only one bromine atom in the Complex II reacts as bromonium cation to afford bromobenzene from PhMgBr.

Different behaviors of the Complex II in the three solvents, namely tetrahydrofuran, ethyl ether, and water, would provide a key to solve this problem. The Complex II is remarkably soluble in THF without any decomposition, but it does not dissolve in ethyl ether.[2] In water, this complex decomposes with release of molecular bromine.[2] The similar complex containing peroxide is not obtained from the reaction in ethyl ether. Since ethyl ether is more weakly basic than THF,[7] the complex containing BPO, if it is formed in ethyl ether, may have a lower electron density around the Mg–atom than in the case of the Complex II itself and may thus make easier the Br–atom to be detached as cationic bromonium ion. The stability of the Complex II itself may thus be ascribed to the strong coordination of THF to Mg–atoms. Another fact that a heavy precipitate appears easily when the ethyl ether solution of PhMgBr is carbonated, can also be ascribed to the easier disproportionation of PhCOOMgBr into $(PhCOO)_2Mg$ and $MgBr_2$ because of the lower coordinating ability of ethyl ether. Thus the complex similar to the Complex II is hard to exist in such a system. The easy releasing of molecular bromine upon treatment of the Complex II with water may be the result that the water molecule replaces the THF molecules and makes stronger the polarity of the Mg-Br bond and finally expels the bromine as bromonium ion. Thus, the different behaviors of the Complex II in the three solvents can be illustrated if the Mg–Br bond in the Complex II is considered to be broken heterolytically to produce bromonium ion.

Another observation which supports the consideration clearly is the fact that reaction of the Complex II with cyclohexene produces 1,2-dibromocyclohexane in the yield as high as more than 85%. Thus, the olefine may be attacked by the bromonium ion, which is produced through the slow electron-transfer process, to give 2-bromocyclohexyl carbonium ion, and this carbonium ion attacks another Mg–Br bond to afford 1,2-dibromide. Therefore, the formation of bromobenzene may be the result of the nucleophilic attack of phenyl anion on the Mg–Br bond. The oxidation of one of the two Mg–Br linkages through the slow electron-transfer process may thus be the characteristic mechanism of the Complex II.

Experimental

Reagents. All the reagents were prepared and/or obtained in the same manner with those used in the preceding paper.[3]

Measurements of Spectra. IR spectra were measured as Nujol-mulls and as THF solutions with Nihon Bunko IR-S-type and DS-401-type spectrometers. Visible absorption spectra were measured with Perkin–Elmer 202-type spectrometer.

Preparation of the Solution of the Complex II. Ten mililiters of stocked solution of PhMgBr in THF (0.57 M) was pipetted into the N_2-purged flask and 20 m*l* of THF was added. The three-way glass-cock was turned and dried CO_2 was introduced with vigorous stirring. The stirring was continued for 30 min after the absorption of CO_2 was completed. The flask was then warmed up to about 50°C for 30 min to expel the excess CO_2 completely with slow nitrogen stream. After the solution was cooled to 0°C, 0.690 g of BPO (0.00285 mol) and 20 m*l* of THF were added successively with gentle stirring. The mixture was stirred at 0°C for 30 min and at room temperature for 90 min. The orange–colored solution of 0.00285 mol of the Complex II in THF (50 m*l*) was thus prepared and was used for the next reaction.

Reaction of the Complex II with PhMgBr. Ten mililiters of PhMgBr solution (0.57 M) was diluted to 30 m*l* and added to the solution of the Complex II prepared above. In the experiments No. 1 and No. 2, the mixing apparatus described in the preceding paper[3] was used. In No. 3, a pressure-equalized dropping funnel was used. In No. 4 and No. 5, a burette equipped with a pressure-equalizing tube was used. All the experiments were conducted under nitrogen stream.

Product Analysis. The reaction mixtures were concentrated to a small volume under reduced pressure, treated with aqueous ammonium chloride, extracted with ethyl ether and washed with aqueous sodium hydrogencarbonate. The ether extracts were dried over anhydrous magnesium sulfate and concentrated for vpc analysis. The ether solution of neutral products was analyzed with Yanagimoto GCG-55A-type and GCG-2-type vapor fractometers. The water extracts were acidified, and the precipitated benzoic acid was extracted with ether, evaporated to dryness and weighed.

Reaction of the Complex II with Cyclohexene. To a 90 m*l* of the orange-colored solution of the Complex II (0.00546 mol), the same moles of cyclohexene in 10 m*l* of THF was added at once at room temperature. One mililiter portions of the reaction mixture were pipetted out at definite time intervals, and titrated with thiosulfate solution according to Wibaut.[8] After about 4 hr, the thiosulfate euqivalent comes down to a value to about 10% of used peroxide, and the color of the reaction mixture faded almost completely. The solution was evaporated to a small volume under reduced pressure, ethyl ether was added, and the pale-yellow crystals were removed by filtration. The filtrate was treated as usual manner, and the neutral part was analyzed again by vpc technique using hexachloroethane as the inner reference. Any product other than 1,2-dibromocyclohexane was not detected.

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[7] H. E. Wirth and P. I. Slick, *J. Phys. Chem.*, **66**, 2277 (1962).

[8] J. P. Wibaut, H. B. van Leewen, and B. van der Wal, *Rec. trav. Chim. Pays-Bas*, **73**, 1033 (1954).