

FORMATION OF COBALT COMPLEXES RESULTED FROM HYDROGEN ABSTRACTION FROM SOLVENT  
BY OXYGEN DEPENDENT HOMOLYSIS OF PHENYLETHYLCOBALOXIME

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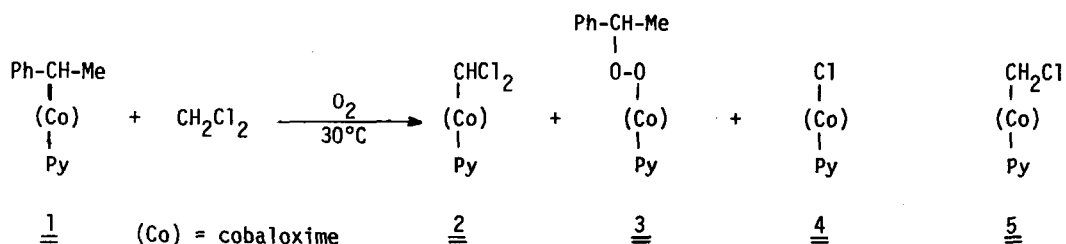
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The homolysis of a Co-C bond accompanied by hydrogen abstraction from environmental molecules giving rise to the new Co-C bond formation with the molecules is of particular interest in connection with the reaction mechanism of the vitamin B<sub>12</sub> dependent dehydrase.<sup>1</sup> It has been known that the homolysis of alkylcobalt complexes which have no hydrogen at the β-position causes the hydrogen abstraction from solvent,<sup>2</sup> yet no information has been available about the formation of new Co-C bond with the solvents.<sup>3</sup> It is also generally believed that the homolysis of alkylcobalt complexes susceptible to the β-elimination does not cause the hydrogen abstraction from the environmental molecules.<sup>3</sup> Alkylcobalt complexes are known well to undergo the homolysis by thermolysis<sup>4</sup> or photolysis.<sup>5</sup> The homolysis of 1-phenylethyl(pyridinato)-cobaloxime (1) is a typical case where the β-elimination occurs.

We wish to report here that the homolysis of 1 in CH<sub>2</sub>Cl<sub>2</sub> in the presence of oxygen leads to the formation of dichloromethyl(pyridinato)cobaloxime (2). This provides the first example of the new Co-C bond formation resulted from the reaction involving the hydrogen abstraction from the environmental molecules by an alkylcobalt complex susceptible to the β-elimination.

A solution of 1 in CH<sub>2</sub>Cl<sub>2</sub> was warmed up to 30°C for 12 h in the presence of oxygen. The reaction mixture was chromatographed on a silica gel column to give the complex 2, orange prisms, mp 210-212° (decomp); NMR (CDCl<sub>3</sub>): δ 2.13 (12H, s, 4 x Me), 5.82 (1H, s, CHCl<sub>2</sub>), 7.3-



-8.5 (5H, m, Py H),<sup>6</sup> together with 1-phenylethylperoxy(pyridinato)cobaloxime (3) and chloro-(pyridinato)cobaloxime (4). Yields of the products are dependent on the amount of oxygen supplied in the reaction system. The complex 2 was not formed in the absence of oxygen, where main isolable products were 4 and chloromethyl(pyridinato)cobaloxime (5). These products are normal ones for the reaction between the solvent and Co(II) species generated on the homolysis.<sup>8</sup> The results are summarized in Table 1. The results indicate that the complex 2 is not formed by the reaction of the solvent with the hydridocobaloxime normally produced on the homolysis of alkylcobaloximes<sup>3,4</sup> and that neither the Co(II) species nor 1-phenylethyl radical is able to abstract hydrogen from the solvent. The existence of nearly equimolar amount of oxygen results in the optimal yield of 2, whereas the higher oxygen pressure leads to the predominant formation of 3 as already reported.<sup>9</sup> On the other hand, the higher oxygen pressure causes the higher rate

Table 1. Thermal Cleavage of 1 in CH<sub>2</sub>Cl<sub>2</sub> (0.07 M)

O <sub>2</sub> Pressure <sup>a</sup> (Torr.)	Additive (mol/mol vs. <u>1</u> )	Reaction Temperature (°C)	Reaction Time (h)	Product (%) <sup>b</sup>			
				<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
0		40 <sup>d</sup>	12	0	0	27	24
1/50		30	12	46	11	28	0
1/50	DBHT <sup>c</sup> (2)	30	24	12	0	20	0
1/10		30	5	23	45	trace	0
1/5		30	4	16	59	trace	0
1/5		40 <sup>d</sup>	3	16	15	13	0
1/5	3 (1)	40 <sup>d</sup>	3	16	17	13	0
1		30	2	10	81	trace	0
N <sub>2</sub> <sup>e</sup>		40 <sup>d</sup>	7	trace	0	23	9
N <sub>2</sub> <sup>e</sup>	DBPO <sup>c</sup> (1.5)	40 <sup>d</sup>	7	17	0	11	6

<sup>a</sup> Pressure 0 refers the degassed condition below  $5 \times 10^{-5}$  Torr. Other pressures were supplied by mixing N<sub>2</sub> and O<sub>2</sub> by means of a gas burette. <sup>b</sup> Yields were determined by isolation (silica gel column chromatography, eluted with gradient mixture of CH<sub>2</sub>Cl<sub>2</sub> and acetone). <sup>c</sup> Abbreviations: DBHT = 3,5-Di-*t*-butyl-4-hydroxytoluene. DBPO = Di-*t*-butylperoxide. <sup>d</sup> Under reflux condition; material balance of the products is not good because of giving rise to a complex mixture but the yield of 2 is not dependent on the temperature change. <sup>e</sup> Nitrogen was prepurified by passing it through a basic solution of hydroquinone.

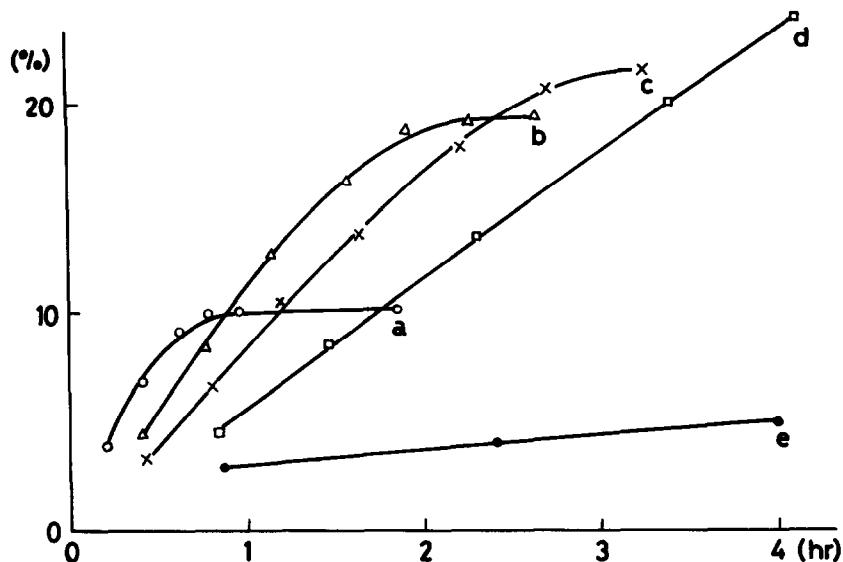


Figure 1. Time course of the formation of 2 on the thermal cleavage of 1 in  $\text{CH}_2\text{Cl}_2$  (0.07 M) at  $30^\circ\text{C}$  under various oxygen pressure (Torr.); (a) 1, (b) 0.2, (c) 0.1, (d) 0.02, (e) 0.02 with DBHT (0.14 M).

of the formation of 2 (Figure 1). These facts clearly indicate that oxygen is essentially required for the formation of 2. Furthermore, the formation of 2 was inhibited by a radical trapping agent, 3,5-di-*t*-butyl-4-hydroxytoluene (Figure 1), suggesting that the reaction involves the hydrogen abstraction by a radical in which oxygen takes part. Complexes 3, 4, and 5 were fairly stable under the reaction conditions. These complexes are therefore not connected with the hydrogen abstraction. When Co(II) species was heated in  $\text{CH}_2\text{Cl}_2$  at  $40^\circ\text{C}$ , a complex mixture containing 4 was obtained but no 2 was detected in the mixture. This excludes the possibility that the Co-C complex formed from the Co(II) species and oxygen<sup>10</sup> may abstract hydrogen from the solvent. The formation of 3 involves the thermal carbon-cobalt bond homolysis followed by the trapping of the alkyl radical by oxygen.<sup>11</sup> The striking drop in the yield of 2 at higher oxygen pressure suggests that 1-phenylethylperoxy radical formed in the course of the formation of 3 is not connected with the hydrogen abstraction. The thermal decomposition of 1 in the presence of di-*t*-butyl peroxide as the source of *t*-butoxy radical gave 2 (Table 1). This would suggest that 1-phenylethoxy radical may be the hydrogen abstraction species for the formation of 2. However, the product from the organic moiety of 1 during the formation of 2 is

mostly styrene. Since 1-phenylethanol does not give styrene under the reaction conditions, it is concluded that the hydrogen abstraction is not caused by the alkoxy radical. Eventually, the mechanism by which the complex 2 is formed from 1 may be rationalized as follows. The reaction of oxygen with hydrido(pyridinato)cobaloxime formed on the homolysis of 1 gives hydrogen peroxide, which is then decomposed to hydroxy radical in the presence of the Co(II) species. The hydroxy radical abstracts hydrogen from the solvent followed by the trapping of dichloromethyl radical by the Co(II) species.

It is also found that the thermolyses of benzyl(pyridinato)cobaloxime in  $\text{CH}_2\text{Cl}_2$  and 1 in  $\text{CHCl}_3$  in the presence of oxygen give 2 and trichloromethyl(pyridinato)cobaloxime, respectively.

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