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Organocobaloximes: synthesis, oxygen insertion and kinetics

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Abstract

A total of 27 organocobaloximes have been synthesised and characterized with three different dioxime ligands, dmgH, chgH and dpgH. Many of the chgH and all the dpgH complexes have been synthesised for the first time. The insertion of molecular oxygen into these organocobaloximes, $RCo^{III}(L_2)B$ [L = dmgH, chgH and dpgH) under thermal and photochemical conditions have been studied. Kinetic studies at ambient temperature under irradiation show that the rate of insertion depends upon the nature of R, L, B and the solvent. The rate follows the order dpgH > chgH > dmgH; Naphthyl > heteroaromaticmethyl > benzyl; piperidine > morpholine > γ-picoline > pyridine > 2-bromopyridine > 2-acetylpyridine; and the rates are faster in acetonitrile than in acetone and chloroform. In methanol, the benzylic cobaloximes exist as an equilibrium mixture of solvated penta-coordinated and hexa-coordinated species and in chloroform these exist as hexa-coordinated species.

Keywords: Organocobaloximes; Dioxygen insertion reactions; Kinetic studies

1. Introduction

Organocobaloximes, $RCo^{III}(dmgH)_2B$ (where R is an organic group, B is the coordinating base) have been extensively studied [1], ever since Schrauzer first highlighted their importance as models of coenzyme B_{12} [2]. Since then it has outgrown its initial relevance and has acquired an independent research field because of its rich chemistry [3]. The key feature of these complexes is the weak Co–C bond ([4]a,b) and this bond in alkyl cobaloximes has been reported to be homolytically cleaved by irradiation with visible light in a manner similar to the activation of vitamin B_{12} by apoenzyme ([4]c,d,e). These compounds find a great use in organic synthesis [5] and in catalysis [6]. Since small structural changes in the molecule have a profound effect on its reactivity, the synthesis of new organocobaloximes continues to attract the attention of the chemists [1,3,7]. The importance of organocobaloximes with ligands other than dmgH has recently been perceived in many reactions in organic synthesis [7,8].

We are, in particular, interested in the reaction of organocobaloximes with molecular oxygen. Reactions involving fixation of O_2 are important not only for a biological system but also for some synthetic processes ([9]a–e). Some reactions of alkylcobaloximes have been reported, e.g. O_2 has been shown to insert into Co–C bond to give a stable 1:1 dioxy adduct ([9]f,g,h).

$$RCo^{III}(dmgH)_2PY + O_2 \rightarrow ROOCo^{III}(dmgH)_2PY$$

Both thermal and photochemical activation of these reactions have been observed. The reaction conditions vary over a wide range depending on the nature of R group, for example, when R is benzyl or allyl the reaction proceeds both under thermal as well as photochemical conditions but when R is alkyl, the photochemical conditions are essential [10]. Stereochemical studies have confirmed that such reactions occur with racemisation at the α carbon [11]. The last review on the insertion of oxygen in to M–C bond giving peroxo complexes was published by Wojcocki [12].

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Most of the insertion studies have been confined to organocobaloximes with dmgH as the equatorial ligand. The photochemical insertion of O_2 into Co–C bond in $[PhCH_2Co(CN)_5]^{3-}$ and [RCo(tpp)] (R = alkyl; TPP = tetraphenylporphyrinato) have also been reported [13]. A number of mechanisms have been proposed including the radical chain reaction, radical cage mechanism, insertion via five co-ordinate species etc. [14]. No one general unified mechanism can be written for these reactions. One possible reason is the lack of organocobaloximes with ligands other than dmgH and the other is the paucity of the precise rate data on such organocobaloximes [9].

Keeping the above in view we report here (a) the synthesis of many new organocobaloximes with chgH and dpgH as the equatorial ligands; and (b) the insertion reaction with molecular oxygen and their rate studies

2. Results and discussion

The reaction of oxygen gas with organocobaloximes (**1**–**27**) in dichloromethane at 0°C and under irradiation proceed smoothly and are complete within 1 h (as judged from TLC). The corresponding dioxy product (**1a**–**27a**) are formed in nearly quantitative yield. Similar results are obtained in the reaction of 2-thienylmethyl-bis(diphenylglyoximato)base cobalt(III) complexes containing various bases like 2-acetylpyridine, 2-bromopyridine, γ-picoline, morpholine, piperidine, ([24]b–f). The characteristics of the organocobaloximes and their inserted products are given in Table 1.

$$\underset{1-27}{RCH_2Co^{III}(L_2)Py} \xrightarrow[0°C]{h\nu/O_2} \underset{1a-27a}{RCH_2OOCo^{III}(L_2)Py}$$

R = Ph

R = 4 Cl–C_6H_4

R = 4 CN–C_6H_4

R = 4 OMe–C_6H_4

R = 3 OMe–C_6H_4

R = 2-thienyl

R = 3-thienyl

R = furfuryl

R = 1 naphthyl

and (**1**–**9**), L = dmgH; (**10**–**18**), L = chgH; (**19**–**27**), L = dpgH

In view of our recent observations ([7]b, [15]) that the alkyl cobaloximes exist as an equilibrium mixture of solvated penta-coordinated and hexa-coordinated species, we have undertaken the preliminary kinetic study both in chloroform as well as in methanol at room temperature. Our results show that in methanol the benzylic cobaloximes behave similarly to alkyl cobaloximes and exist as an equilibrium mixture of five and six co-ordinated species, with equilibrium largely to the right.

$$RCH_2Co–(L_2)Py \Leftrightarrow RCH_2Co(L_2)\{solvated\} + Py$$

The evidence for this equilibrium is shown in Fig. 1 which depicts the changes in the appearance of the CT band on addition of increasing quantities of pyridine to a solution of $PhCH_2Co(dmgH)_2Py$ in methanol. Similar changes have been observed earlier by Brown et al. in aqueous solutions [16]. The shape of the CT band (Fig. 1 saturation curve) is similar to the one in chloroform. Furthermore the band in chloroform does not change in shape on the addition of a large excess of pyridine. In another experiment when the insertion is carried out in the presence of 2-acetyl pyridine (3–4-fold) in chloroform, the insertion product does not contain any 2-acetylpyridine. This further confirms that the axial base pyridine does not come off at any stage during the insertion.

These results clearly show that the species exists as a hexa-coordinated benzyl (pyridine) cobaloxime in chloroform. ChgH and dpgH complexes behave similarly (Fig. 1). A similar observation is made in the ^{1}H-NMR study. The species exist as six coordinated $RCH_2Co(L_2)Py$ in $CDCl_3$ (the solvent used for NMR) as the cobalt bound methylene as well as the dmgH–Me proton resonances did not shift on the addition of a large excess of pyridine directly to the NMR sample.

The detailed kinetic study of the molecular insertions have been carried out in chloroform using UV-vis spectrophotometer. Spectrophotometery has shown that for every molecule of oxygen consumed, one molecule of the complex is transformed ([14]a). Thus the intensity of the characteristic band at around 420 nm decreases proportionally with the quantity of oxygen consumed. The absorbance (A_t) is noted down at different intervals and the concentration of the product (C_t) at any time (t) is calculated using the equation $C_t = A_0 - A_t/\varepsilon - \varepsilon_A$ where A_0 and A_t are absorbances at time $t = 0$ and at time t and ε and ε_A are molar extinction coeffcients of the initial and final complex. The following findings are noteworthy from the overall insertion studies. Some of these findings are similar to earlier studies ([9]f, [14]).

(A) The reactions do not proceed in the dark at 0°C; (B) the reactions stop as soon as the irradiation is stopped; (C) the best temperature for insertion is 0°C, though the reaction proceeds at ambient temperature also but the time taken is more than the reaction at 0°C (TLC inference only). (D) A plot of log $(C_0 - C_t)$ against t is linear indicating the first order kinetics. The results point to the overall order of reaction as 2, i.e. first order with respect to both the complex and oxy-

Table 1
The yield, spectroscopic and R_f data for $RCH_2CoI^{III}(L_2)Py$ and $RCH_2OOCo^{III}(L_2)Py$[a]

Composition yield	Yield (%)[b]	^{1}H-NMR chemical shifts, δ (ppm), $CDCl_3$							λ_{max} (nm)[c]	R_f[d]
		Aromatic	CH_2Co (s)	L	Pyridine			OH···H		
					α	γ	β			
2a		6.87–7.21	4.31	2.21,2.31	8.38	7.62	7.28	17.81		0.18
3a		6.87	4.31	2.21, 2.31	8.34	7.62	7.28	17.81		0.17
4a		6.65–7.20	4.31	2.15, 2.25	8.35	7.59	*	18.66		0.17
5a		6.73–7.36	4.31	2.28, 2.38	8.41	7.54	*	18.00		0.16
9a		7.00–7.97	4.86	2.21	8.48	8.08	*	17.81		0.11
10	74	6.67–7.12	2.90	1.46 2.48,	8.60	7.62	7.38	17.81	245, 466.7	0.62
10a		6.88–7.50	4.35	1.57, 2.80	8.39	7.65	*	—		0.18
11	71	6.59–7.20	2.80	1.51, 2.50	8.52	7.69	7.25	17.69	244, 464.8	0.59
11a		6.88–7.38	4.31	1.60, 2.82	8.38	7.71	*			0.18
12	76	6.88–7.50	2.76	1.52, 2.51	8.62	7.66	*	17.69	231, 461.6	0.58
12a		6.88–8.12	4.37	1.59, 2 71	8.35	*	*			0.18
13	62	6.60–699	2.91	1.47, 2.49	8.53	7.53	7.28		240, 468.0	0.59
13a		6.56–7.50	4.38	1.56, 2.88	8.12	7.81	*			0.18
14	64	6.25–7.06	2.87	1.47, 2.49	8.56	7.71	7.29	17.19	243.5, 466.7	0.63
14a		6.56–7.52	4.38	2.88	8.12	7.81	*			0.20
18	72	6.88–8.12	3.40	1.26, 2.29	8.57	*	*	17.94	231, 467.2	0.60
18a		6.80–8.75	5.00	1.62, 2.81	9.06	*	*			0.18
19	70	6.71–7.68	3.55	*	8.97	7.87	*	18.68	244, 472.9	0.34
19a		6.84–7.55	4.71	*	8.84	7.87	*	18.90		0.14
20	75	6.64–7.48	3.36	*	8.87	7.74	*	18.68	236.5, 471.9	0.34
20a		7.19–7.27	4.55	*	8.72	7.42	*	18.75		0.14
21	72	6.58–7.55	3.35	*	8.77	7.81	*	18.68	229, 472.5	0.30
21a		7.16–7.24	4.57	*	8.67	7.76	*	18.72		0.10
22	71	7.00–7.81	3.41	*	8.87	7.81	*	18.74	261.5, 472.6	0.30
22a		7.16–7.81	4.63	*	8.67	7.74	*	18.76		0.11
23	70	6.76–7.50	3.41	*	8.81	7.72	*	18.74	245, 472.6	0.30
23a		7.60–7.81	4.64	*	8.67	7.61	*	18.76		0.10
24	78	6.71–7.61	3.68	*	8.97	7.81	*	18.62	245	0.36
24a		6.77–7.50	4.84	*	8.77	7.80	*	18.88		0.16
25	76	6.64–7.68	3.55	*	8.97	8.01	*	18.75	242.5, 472.4	0.36
25a		7.17–7.25	4.60	*	8.69	7.75	*	18.68		0.16
26	78	6.77–7.74	3.32	*	8.85	7.87	*	18.75	244.5	0.31
26a		7.21–7.42	4.54	*	8.68	7.75	*	18.75		0.11
27	70	6.66–8.00	4.03	*	8.92	8.02	*	18.38	226sh, 472.5	0.30
27a		6.84–7.81	5.03	*	8.74	7.87	*	18.65		0.10

[a] All the complexes give the satisfactory elemental analysis.
[b] Yields for the inserted products are almost quantitative in each case. The known compounds are not listed, ([9]f, [30]).
[c] The first value refers to MLCT and the second one to Co–C CT band.
[d] Ethylacetate is the eluent for the compounds **1**–**18** and **1a**–**18a** and a mixture of EtOAc:CCl_4 (1:9) is used for the compounds **19**–**27** and **19a**–**27a**.
[e] Merge with aromatic.

gen. (E) The rate of reaction is slowed down in the presence of radical inhibitor like galvinoxyl; (F) the rate of insertion changes as the equatorial ligand is changed and it follows the order dpgH > chgH > dmgH in all cases. (G) The solvent affects the rate and it follows the order acetonitrile > acetone > chloroform; (H) the reaction proceeds faster as the axial base strength increases; 2-acetylpyridine < 2-bromopyridine < pyridine < γ-picoline < morpholine < piperidine; (I) the rate changes with the change in R group and it follows the order naphthyl > heteroaromaticmethyl > benzyl for the three series of complexes. Among the benzyls, *p*-methoxybenzyl has the highest rate and among the heteroaromaticmethyl groups it follows the order 2-thienylmethyl > 3-thienylmethyl > furfuryl for all the three series of complexes. It seems clear that the rate of insertion depends upon various factors including the nature of R, L, B and the solvent.

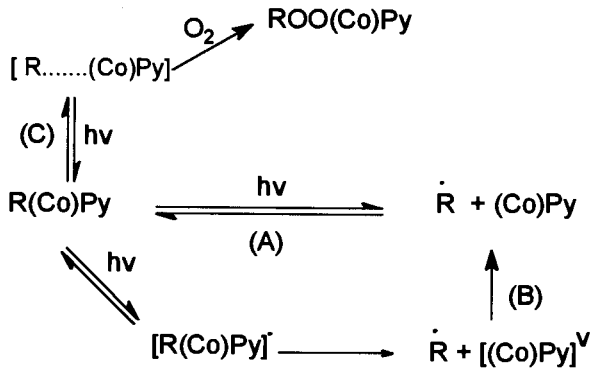
Oxygen insertion into M–C bond is a reaction which occurs with remarkably a wide range of organometallic compounds. Both thermal as well as photochemical activation of these insertions have been observed in the Co–C bond of organocobalt complexes. The results in the photochemical reactions are much more difficult to

interpret owing to the greater complexity of this reaction compared to thermal reactions; the exact role of light in these reactions is not known. Many suggestions have been made by various workers, e.g. Schrauzer has proposed, based in part on MO calculations, that photolysis of alkyl cobaloximes leads to excitation and subsequent homolytic cleavage of the Co–C bond [17]. Giannotti and coworkers have suggested that photolysis with light in the charge transfer region (about 450 nm) leads to the expulsion of the axial base ligand as the primary photochemical process [18]. The Co–B bond is reformed after the insertion has taken place.

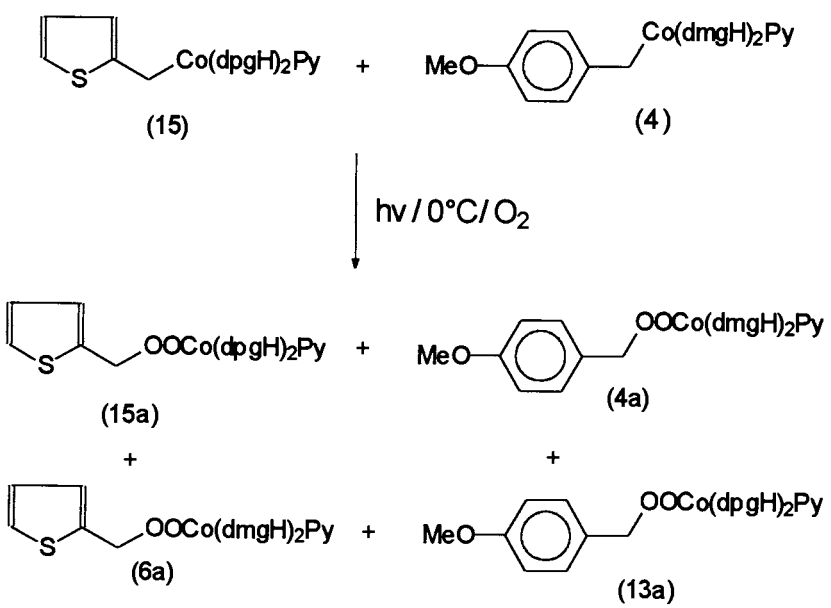
Several mechanisms including a radical chain mechanism can be envisaged for the insertion of oxygen into Co–C bond in organocobaloximes. Such radical chain reactions generally require induction period and once these start they proceed to completion without the external stimulation by light. However, in view of the experimental observations in the present study that (a) there is no induction period; (b) the reaction stops as soon as the light stimulation is stopped; (c) the organocobaloximes in the absence of oxygen are stable at 30°C, i.e. at a temperature where the insertion occurs readily as shown by kinetics, we rule out the participation of such a chain mechanism.

We have not considered any mechanism involving thermal conditions since no insertion has been observed in the dark under thermal conditions,. Similarly, any mechanism which involves the loss of pyridine at any stage in the photochemical process has also been ignored. Even if such a base off process was operating then the rate of insertion should have increased with the decrease in base strength, however a reverse order has been observed in the present study.

Among the three other possibilities A, B and C, the basic difference in these mechanisms is that in (A), the free radicals R and (Co)Py are involved. R picks up O_2 and the adduct combines with (Co)Py to give the insertion product. In this the stability of R plays an important role and should affect the rate. Mechanism (C) on the other hand does not involve a complete rupture of Co–C bond, the resulting radical pair (R…Co) within the solvent cage on reaction with O_2 gives the final inserted product. In this case the nature of solvent should affect the rate. Such a mechanism has been proposed by many workers [19–21].



It seems difficult to distinguish between these possibilities without doing a more detailed studies but since the solvent and the R group do affect the rates in these reactions, it looks certain that the mechanism (A) and (C) are operative. It is, however, very difficult to know their relative contribution to the overall rate. The formation of cross insertion products further suggest that a complete rupture of bond takes place, i.e. the mechanism (A) is operating.



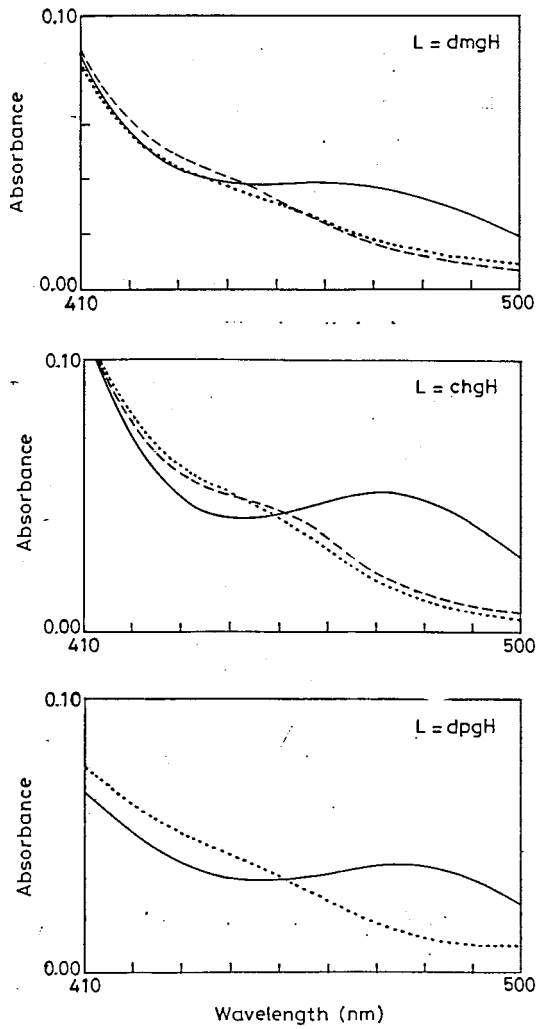


Fig. 1. Effect of the addition of pyridine (— 0.0 M, ---- 10^{-3} M, ··· 10^{-2} M saturation curve) to a 10^{-5} M solution of benzyl(L_2)Py in methanol (L = dmgH (1), chgH (10); for the complex L = dpgH (19), the plot is only qualitative.

Finally, the change in the insertion rate for a given compound having the same R and B but different equatorial ligand L is hard to explain. One of the contributing factors may be the *cis* influence exerted by the bulkier equatorial ligand on the Co–C bond. We find that the magnitude of Δidp is significantly larger [0.56–0.92] ppm than Δich [0.00–0.34] ppm in all cases where $\Delta idp = \delta i_{dpgH} - \delta i_{dmgH}$ and $\Delta ich = \delta i_{chgH} - \delta i_{dmgH}$ and δi is the chemical shift. If this is taken to be as the extent of *cis* influence, as described in earlier papers ([7]b, [16,22]), then the order of *cis* influence follows the order dpgH > chgH ≅ dmgH. The extent of *cis* influence is felt most on the Co–CH_2 followed by P_α.

3. Experimental

Chlorocobaloxime, $ClCo^{III}(L_2)Py$ (L = dmgH, chgH and dpgH) [15]. 2-Chloromethylthiophene, 3-bromomethylthiophene, furfurylbromide, 4-cyanobenzylbromide, 4-methoxybenzylbromide, 3-methoxybenzylbromide were synthesised according to the published procedures [23–28]. Diphenylglyoxime, 1,2-cyclohexanedionedioxime and all the other halides were obtained from Aldrich and were used as such.

The organocobaloximes were synthesised by a general procedure detailed earlier in many papers ([7]b, [15]) and involves the reaction of cobaloxime(I), with the corresponding benzylic halide. Cobaloxime(I) was prepared in situ by the $NaBH_4$ reduction of chlorocobaloximes in aqueous methanol under strict oxygen free atmosphere. The work-up procedure was similar to the ones described earlier ([7]b, [15]). The crude products were purified by column chromatography as described earlier for alkyl cobaloximes [15].

2-Thienylmethyl$Co^{III}(dpgH)_2B$ [B = 2-acetylpyridine, 2-bromopyridine, picoline, morpholine, piperidine] were prepared by replacing the aqua group from 2-thienylmethyl$Co^{III}(dpgH)_2H_2O$. In a typical experiment morpholine (0.029, 0.23 mmol) in acetone (1 ml) was added dropwise to a solution of 2-thienylmethyl(aquo)cobaloxime (0.129, 0.18 mmol) in acetone (3 ml). The reaction mixture was stirred in dark in an inert atmosphere. The completion of the reaction was checked with TLC on silica gel using ethyl acetate:CCL_4 in 1:9 ratio. The wine red coloured solution fumed orange within minutes and the orange precipitate which formed were filtered, washed with acetone (2 × 2 ml) and dried in vacuum over P_2O_5. Yield 68%

The aqua complex was prepared from the corresponding pyridine complex following the literature procedure [29]. In a typical experiment, 2-thienylmethyl$Co^{III}(dpgH)_2Py$ (214 mg 3 mmol) was dissolved in acetone (30 ml). To this was added 5 ml of water and 248 mg of Dowex 50w-x ion exchange resin (H^+ form) and the mixture was stirred for 16h in the dark. The mixture was filtered and the filtrate was evaporated to 510 ml, cooled in ice and filtered to produce orange powder which was washed with cold water and dried in vacuo over P_2O_5. Yield 80%

3.1. Physical measurements and instruments

The ^{1}H-NMR spectra were recorded on a Bruker WP-80 FT NMR machine. UV-vis absorption spectra were recorded on Shimadzu UV-190 spectrometer at ambient temperature. The elemental analysis were undertaken at the Regional Sophisticated Instruments Centre, Lucknow.

3.2. General procedure for oxygen insertion under photochemical conditions

In a typical experiment a solution of organocobaloxime (0.2 mmol in 100 ml dichloromethane) at 0°C was irradiated with 2 × 200 W tungsten lamps kept at a distance of ca. 10 cm. and pure oxygen was bubbled into this solution. The progress of the reaction was monitored by TLC on silica gel using ethylacetate (dmgH and chgH) or 1:9 ethylacetate/CCl_4 mixture (dpgH) as the eluent. The reaction was complete within 2 h in all cases. There was a distinct colour change from yellow-orange to dark brown at this stage. At the end of reaction, the solvent was stripped off and the crude product was purified on silica gel column using ethyl acetate as the eluent. The yields were almost quantitative in all cases.

3.3. Oxygen insertion in presence of 2-acetylpyridine

The same general procedure as above was followed except that 2-acetylpyridine (3–4-fold excess) was added to the reaction mixture. After the completion of the reaction, the solvent was completely evaporated and the solid was washed three to four times with diethylether. The ^{1}H-NMR on the residue showed that it had no 2-acetylpyridine. The ether on evaporation gave back all the 2-acetylpyridine.

3.4. Cross insertion reaction between 2-thienylmethyldpgH complex (**15**) and 4-methoxybenzyldmgH complex (**4**) in dichloromethane at 0°C

The general procedure is same as outlined above. In a typical experiment, a solution of two organocobaloximes 2-thienylmethyl dpgH complex (**15**, 0.424g, 0.59 mmol) and 4-methoxybenzyl dmgH complex (**4**, 0.291g, 0.59 mmol) in 300 ml dichloromethane was irradiated with 2 × 200 W tungsten lamps at 0°C. After completion of the reaction the semi-solid mixture, dissolved in minimum amount of chloroform, was loaded on silica gel column (100–200 mesh) pre-eluted with chloroform. The polarity of the solvent was carefully increased with ethylacetate (0–10%). The first fraction contained organic product followed by dpgH complexes and finally the dmgH complexes.

3.5. Kinetics of oxygen insertion under photochemical conditions at 30°C procedure

Pure oxygen was bubbled through chloroform or methanol (100 ml) for 2 h and a solution of organocobaloxime (3–4 mg) was made (10–5 M) in the above solvent. This solution was taken in the spectrophotometric cell, stoppered and was irradiated with 200 W tungsten lamp at 30°C. The progress of the reaction was monitored by measuring the absorbance at 420 nm at intervals.

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