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Molecular oxygen insertion into organocobaloximes: kinetics and decomposition studies

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Abstract

The insertion of molecular oxygen into the Co–C bond in organocobaloximes under thermal and photochemical conditions has been studied. Kinetic studies have shown that the reaction is of first order with respect to both the complex and oxygen. The thermal decomposition of the organocobaloximes and their insertion products has been carried out in benzene and methanol and a mechanism is proposed for the decomposition.

Introduction

There is much interest in the reactions between cobalt complexes and molecular oxygen. The latter has been shown to insert into the Co–C bond of an organocobaloxime to give a stable 1 : 1 dioxy adduct [1,2] (Eq. 1):

$$RCo^{III}(dmgH)_2Py + O_2 \rightarrow ROOCo^{III}(dmgH)_2Py \quad (1)$$

The conditions needed for the reaction vary over a wide range. For example, when R is benzyl or allyl group, the insertion proceeds either thermally in the dark or photochemically, but when R is alkyl, no reaction takes place even at slightly elevated temperatures, except under irradiation [3,4]. The reaction of molecular oxygen with organocobaloximes is of special interest in view of its generality and the ease with which it takes place. There is, in fact, no report of a cobaloxime which does not give the dioxy adduct under the above conditions. Photochemical insertions of O_2 into Co–CH_2 bonds of $[PhCH_2Co(CN)_5]^{3-}$ and [RCo(tpp)] (R = alkyl, tpp = tetraphenylporphinato) have also been reported [5]. Wojcicki has reviewed the information on insertion of O_2 into M–C bonds [6]. Stereochemical studies on the optically active organocobaloximes has confirmed that such insertions occur with racemisation at the α-carbon [7].

The mechanism of the reaction of oxygen with organocobaloximes has not been well defined because of the paucity of precise kinetic data The kinetic studies by

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Jenson and Kiskis [7a], showed that the photochemical reactions take place after dissociation of the axial base ligand, as suggested earlier by Giannotti and co-workers [7c], whereas the photochemical reaction involves the hexacoordinate complex. The kinetic studies of the oxygen insertion, both thermal and photochemical, into $RCo(dmgH)_2L$ (R = alkyl, L = Py, H_2O) show first order dependence on the cobalt complex and on O_2 [8]. In the photochemical reaction the presence of an excess of L retards the reaction in ethanol and water and the variation of rate with R is not large, suggesting that the role of $h\nu$ is not to induce Co–R homolysis. Several mechanisms including radical chain and radical cage mechanisms were considered [8]. Only very limited studies have been made on the decomposition of the insertion products [9,10].

We describe below the results of a study of the reaction of molecular oxygen with some heteroaromatic methyl cobaloximes under thermal and photochemical conditions. The decompositions of the organocobaloximes and their insertion products in benzene and methanol have also been examined.

Results

The reaction of oxygen gas with 2-thienylmethyl cobaloxime (**1**) in CH_2Cl_2 at 0 °C under irradiation proceeds smoothly, and is complete within 1 h (as judged from TLC). The corresponding dioxy product (**1a**) is formed in nearly quantitative yield. Similarly, the reactions of 3-thienylmethyl, furfuryl, 3-furylmethyl, 2-benzofurylmethyl, 2-thianaphthylmethyl and 3-thianaphthylmethyl (**2–7**) under identical reaction conditions give the corresponding dioxy adducts (**2a–7a**) in almost quantitative yield. The reactions of the corresponding cobaloximes having cyclohexane dionedioximato (1 −) as the equatorial ligand (**8–14**) are faster, and again give the corresponding dioxy adducts in nearly quantitative yield. Similar results were obtained in the reactions of 2-thienylmethyl bis(dimethyl glyoximato) base cobalt(III) complexes (**15–17**) containing various other axial bases, such as picoline, morpholine and piperidine (Eq. 2 and Table 1).

$$\underset{\textbf{(1–17)}}{RCH_2Co^{III}L_2B} + O_2 \xrightarrow[0\,^\circ C]{h\nu} \underset{\textbf{(1a–17a)}}{RCH_2OOCo^{III}L_2B} \qquad (2)$$

RCH_2 =
2-thienylmethyl
3-thienylmethyl
furfuryl
3-furylmethyl
2-benzofurylmethyl
2-thianaphthylmethyl
3-thianaphthylmethyl

1–7: L = dmgH, B = Py; **8–14**: L = chgH, B = Py; **15–17**: RCH_2 = 2-thienylmethyl, L = dmgH, B = γ-picoline, morpholine or piperidine.

The following findings emerged from the study. Some similar findings were made previously [8a,8b].

(i) The reactions do not proceed in the dark at 0 °C; (ii) the reactions stop as soon as the irradiation is stopped; (iii) the rate of the reaction is lowered by galvinoxyl and increased by the addition of $Co^{II}(dmgH)_2Py$ dimer; (iv) the reactions become faster as the axial base strength increases; (v) the best temperature for insertion is 0 °C; (vi) when the reactions are carried out in the dark in refluxing dichloromethane, no insertion product is formed even after 20 h. However, if reaction is prolonged for 40 h, homolysis of the Co–C bond followed by atom abstraction from the solvent leads to the formation of three new cobaloximes in the ratio 6:3:1, and these have been partially characterised. Two of them are $ClCo^{III}(dmgH)_2Py$ and $CHCl_2Co^{III}(dmgH)_2Py$ (^1H NMR ($CDCl_3$): 2.13(s), 5.82(s), 7.3–8.5(m)). The atom abstraction process is much faster in chloroform as solvent (4 h, 45 °C); one of the major products is identified as $CCl_3Co^{III}(dmgH)_2Py$ (^1H NMR ($CDCl_3$): 2.36(s); 7.20–8.18(m)).

The kinetics of these reactions were studied by UV/VIS spectrophotometry. The concentration of the product (C_t) at any time (t) is calculated from the equation $C_t = A_0 - A_t/E - E_A$ where A_0 and A_t are absorbances at $t = 0$ and at any time t and E and E_A are molar extinction coefficients of the initial and the final complex. A plot of log ($C_0 - C_t$) against t for complexes **1**, **15**, **16**, **17** is linear, indicating first order kinetics, when the concentration of the dissolved oxygen is kept constant by

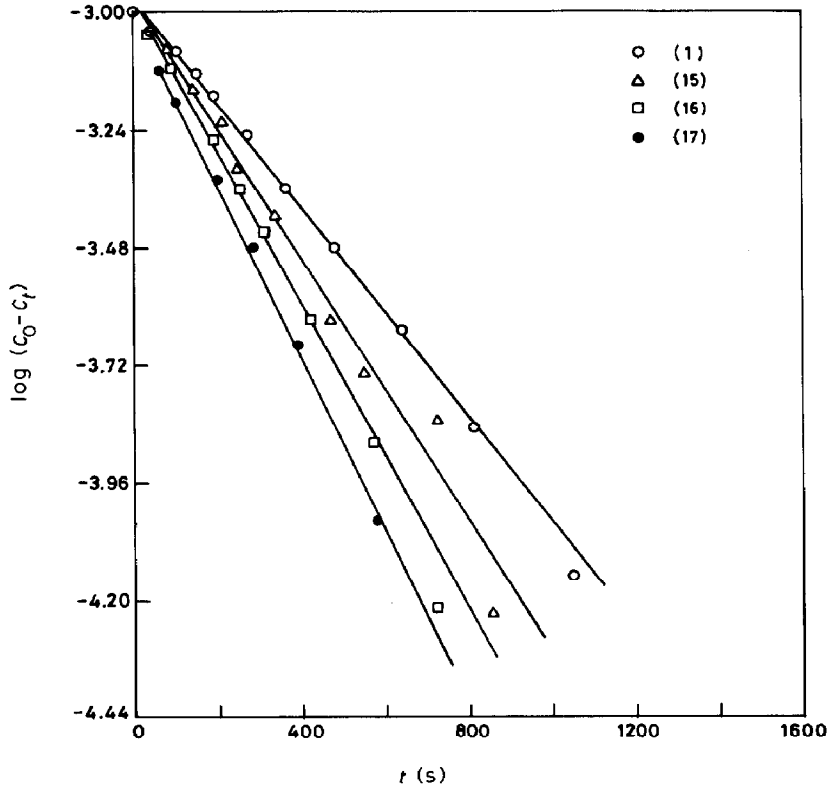


Fig. 1. Plot of log ($C_0 - C_t$) versus t for oxygen insertion in EtOH at 30 °C.

Table 1

Spectroscopic data for $RCH_2Co^{III}(L_2)B$ (**1–17**) and their inserted products $RCH_2OOCo^{III}(L_2)Py$ (**1a–17a**)

Compound	^1H NMR chemical shift, δ [a]				IR, λ, nm (log ϵ) [b]
	Aromatic	CH_2	dmgH/chgH	Base	
1	6.65, 7.00	3.00	2.05	7.20, 7.65, 8.50	385(3.42), 281(3.12) 240(3.49)
1a	6.80, 7.15	4.45	2.25, 2.35	7.15, 7.60, 8.30	237(3.28), 247(3.42), 322(2.92)
2	6.65, 7.20	2.85	2.00, 2.10	7.30, 7.70, 8.50	359(3.20), 277(3.21), 239(3.60)
2a	7.15, 7.25	4.30	2.25, 2.35	7.10, 7.60, 8.30	231(3.34), 244(3.51), 312(2.96)
3	6.00, 7.40	2.40	2.00	7.30, 7.75, 8.60	383(3.39), 284(3.18) 239(3.58)
3a	6.15, 7.15	4.25	2.30, 2.40	7.15, 7.60, 8.30	224(3.11), 359(2.86), 316(2.52)
4	6.00, 7.12	2.55	2.00, 2.10	7.15, 7.75, 8.40	348(3.22), 286(3.31), 238(3.56)
4a	6.30, 7.20	4.15	2.25, 2.35	7.20, 7.60, 8.25	242(2.98), 254(3.20), 324(2.61)
5	6.39, 7.06, 7.18, 7.44	2.75	1.97	7.30, 7.75, 8.55	298(4.68), 282(4.71), 242(5.0)
5a	6.53, 7.19 7.33–7.79	4.36	2.26, 2.34	[c], [c], 8.35	247(5.18), 284(4.86), 305(4.71), 545(2.83)
6	6.94, 7.22, 7.60	3.02	2.00	7.30, 7.70, 8.55	300(4.00), 260(4.41), 257(4.48), 249(4.46), 242(4.45)
6a	7.09, 7.21–7.31, 7.86	4.62	2.34, 2.44	[c], 7.70, 8.45	230(4.58), 245(4.60), 253(4.61), 256(4.57), 300(4.23), 555(2.30)
7	7.04–7.80	3.04	1.85, 1.95	[c], [c], 8.45	295(3.76), 260(4.26), 257(4.34), 249(4.30), 242(4.28)
7a	7.16–7.40, 7.64–7.90	4.60	2.24	[c], [c], 8.40	243(4.30), 250(4.34), 255(4.28), 295(3.90), 547(2.15)
8	6.72, 7.05	3.04	1.36–1.80, 2.40–2.70	7.25, 7.65, 8.50	365(2.91), 315(3.13), 247(3.57)
8a	6.90, 7.16	4.50	1.50–1.90, 2.66–2.84, 2.90–3.06	7.25, 7.70, 8.40	250(4.41), 3.13(4.03), 553(2.39)
9	6.74, 6.98	2.82	1.60, 1.90–2.10	7.30, 7.70, 8.55	463(2.94), 315(4.04), 243(4.46)
9a	7.02, 7.16, 7.24	4.36	1.40–1.82, 2.56–2.80, 2.84–3.00	7.25, 7.70, 8.40	249(4.44), 305(4.04), 558(2.30)
10	6.06	3.54	1.40–1.98, 2.55–2.75	7.20, 7.65, 8.50	308(3.67), 245(3.95)
10a	6.24, 7.26	4.32	1.36–1.86, 2.64–2.82, 2.88–3.10	7.25, 7.70, 8.40	252(4.46), 315(4.15), 558(2.34)
11	6.13, 7.16–7.49	2.60	1.30–1.70, 2.30–2.90	[c], 7.75, 8.60	458(2.98), 345(3.61), 235(4.35)

Table 1 (continued)

Compound	^{1}H NMR chemical shift, δ [a]				IR, λ, nm (log ϵ) [b]
	Aromatic	CH_2	dmgH/chgH	Base	
11a	6.29, 7.26	4.03	1.28–1.90, 2.32–3.10	7.25,7.70, 8.35	247(4.40), 305(3.98)
12	6.40, 7.08, 7.18, 7.28, 7.42	2.80	1.28–1.84, 2.36–2.58	7.30, 7.75, 8.55	305(4.11), 280(4.17), 218(5.10)
12a	6.58, 7.20, 7.38, 7.50	4.48	1.40–1.90, 2.60–2.84, 2.90–3.20	7.25, 7.70, 8.45	247(5.18), 284(4.86), 305(4.71), 545(2.83)
13	6.98, 7.20, 7.29, 7.62	3.06	1.16–1.86, 2.30–2.64	7.30, 7.70, 8.55	303(4.32), 253(4.56), 228(4.59)
13a	7.32, 7.46, 7.54, 7.72, 7.96	4.58	1.42–1.82, 2.62–2.84, 2.86–3.14	7.30, [c], 8.35	230(4.58), 245(4.60), 253(4.61), 256(4.57), 300(4.23), 555(2.30)
14	7.31–7.60, 7.69–8.0	3.13	1.00–1.30, 2.35–2.63	[c], [c], 8.60	390(0.25), 293(1.00), 235(0.26), 213(0.45)
14a	7.30–7.60	4.59	1.40–1.86, 2.40, 2.64–3.16	[c], 7.80, 8.40	213(2.65), 245(2.45)
15	6.63, 7.10	2.97	2.00	7.10, 8.48, 2.25	375(3.69), 280(4.04), 238(4.43)
15a	6.89, 7.00–7.34	4.49	2.24, 2.34	[c], 8.26	568(2.48), 303(4.12), 249(4.39)
16	6.62, 7.06	2.86	2.15	2.26–2.78, 3.20–3.93	375(3.62), 280(3.92), 235(4.28)
16a	7.16, 7.63	4.73	2.43	2.16, 2.33–2.72, 3.03–3.85	303(4.12), 255(4.25)
17	6.61, 7.09	2.93	2.06	1.03–1.87, 1.87–2.36	379(3.79), 285(4.08), 238(4.39)
17a	6.90, 7.22	4.39	2.49	1.06–1.85, 2.16–3.00	558(2.44), 283(4.16), 245(4.39)

[a] In $CDCl_3$, TMS internal standard. [b] In CH_3OH. [c] Me resonance of γ-picoline is obscured under dmgH resonance.

continuous bubbling at a fixed pressure (Fig. 1) whereas there is a linear relationship between $1/(C_0 - C_t)$ and t when the amount of oxygen is kept fixed (in the way described in the experimental section). The results indicate that the overall order of reaction is 2; that is, first order with respect to both complex and oxygen.

Furthermore, it can be seen from Table 2 and 3 that (a) as the axial base strength increases, the rate of the reaction increases in the order piperidine > morpholine >

Table 2

Comparison of the rates of reaction of the various cobaloximes

2-$C_4H_3OCH_2Co$ (**3**)	>	2-$C_4H_3SCH_2Co$ (**1**)
2-$C_8H_5OCH_2Co$ (**5**)	>	2-$C_8H_5SCH_2Co$ (**6**)
3-$C_4H_3SCH_2Co$ (**2**)	>	2-$C_4H_3SCH_2Co$ (**1**)
3-$C_8H_5SCH_2Co$ (**7**)	>	2-$C_8H_5SCH_2Co$ (**6**)
2-$C_4H_3OCH_2Co$ (**3**)	>	2-$C_6H_5OCH_2Co$ (**5**)
2-$C_4H_3SCH_2Co$ (**1**)	>	2-$C_8H_5SCH_2Co$ (**6**)
2-$C_4H_3OCH_2Co$ (**3**)	>	3-$C_4H_3OCH_2Co$ (**4**)

Co = $Co^{III}(dmgH)_2Py$

Table 3

Rate constants ($K_{obs} \times 10^4$) [a] for O_2 insertion into cobaloximes $RCH_2Co^{III}(L_2)B$ in EtOH

Compound no.	RCH_2	L	B	$K_{obs} \times 10^4$, sec^{-1}
1	2-thienylmethyl	dmgH	Py	25
2	3-thienylmethyl	dmgH	Py	28
3	furfuryl	dmgH	Py	26
4	3-furylmethyl	dmgH	Py	22
5	2-benzofurylmethyl	dmgH	Py	23
6	2-thianaphthylmethyl	dmgH	Py	15
7	3-thianaphthylmethyl	dmgH	Py	16
8	2-thienylmethyl	chgH	Py	30.6
10	furfuryl	chgH	Py	31.7
15	2-thienylmethyl	dmgH	γ-picoline	30.6
16	2-thienylmethyl	dmgH	morpholine	35
17	2-thienylmethyl	dmgH	piperidine	40

[a] Rate $= K[RCH_2Co^{III}(L_2)B][O_2] = k_{obs}[RCH_2Co^{III}(L_2)B]$.

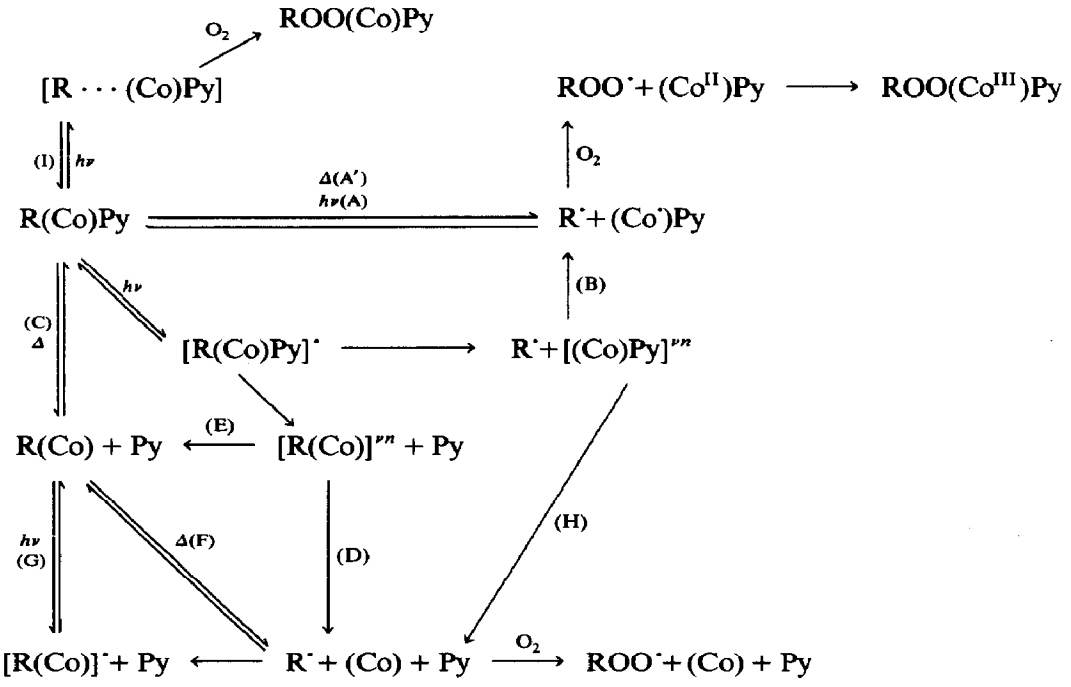
γ-picoline > pyridine; (b) the change in the rate of reactions is much less distinct but still perceptible, and follows a definite order, when the axial R group is varied; (c) heteroatomic methyl cobaloximes having cyclohexane dionedioximate (1 −) as the equatorial ligands undergo oxygen insertion faster than the corresponding cobaloximes having dimethylglyoximate (1 −) as the equatorial ligands (**8** > **1** and **10** > **3**).

Discussion

Oxygen insertion into M–C bonds takes place with a remarkably wide range of organometallic compounds [11–17]. Both thermal and photochemical activation of such insertions have been observed in the case of the Co–C bond of organocobalt complexes [8]. Studies by Schrauzer [18], Giannotti [19], Gaudemer [8] and their coworkers are especially noteworthy. Several mechanisms can be envisaged for such insertion reactions [7a] as depicted in Scheme 1. A radical chain mechanism is also conceivable but is ruled out by the experimental observations.

Some of the mechanisms given in Scheme 1, can be eliminated on the basis of the simple experimental observations. For example, no mechanisms involving thermal activation and no photochemical processes involving loss of pyridine are considered. Thus only the mechanisms A, B and I remain as possibilities. It is difficult to decide finally between these mechanisms without a much more detailed study, but, the following analysis is justified.

The essential difference between mechanisms A, B and I is that in A, the free radicals R$^\cdot$ and (Co$^\cdot$)Py are involved. R$^\cdot$ picks up O_2 and the adduct combines with (Co$^\cdot$)Py to give the insertion product. The stability of the organic free radical R$^\cdot$ plays an important role and should affect the rate of insertion in such a mechanism. On the other hand, mechanism I does not involve a complete rupture of Co–C bond, the resulting (R · · · Co) radical pair within the solvent cage on reaction with O_2 gives the final inserted product. Such a mechanism involving the (R · · · Co) pair in the solvent cage has been suggested by many authors in the light of their ESR



Scheme 1

and combined ESR-spin trapping [20,21] and flash photolysis studies [22]. We prefer this mechanism in view of the observation that: (a) the variation in the rate of insertion with the change in R group is small, suggesting that complete rupture of Co–C bond may not be the slow step, and (b) the rate law corresponding to this mechanism is:

$$\text{rate} = \frac{k_1 k_2 [\text{RCo(dmgH)}_2\text{B}][\text{O}_2]}{k_{-1} + k_2[\text{O}_2]}$$

where K_1, K_{-1} and K_2 refer to

$$\text{RCo}^{\text{III}}(\text{dmgH})_2\text{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\text{R} \cdots \text{Co(dmgH)}_2\text{B}$$

$$[\text{R} \cdots \text{Co(dmgH)}_2\text{B} + \text{O}_2 \xrightarrow{k_2} \text{ROOCo}^{\text{III}}(\text{dmgH})_2\text{B}$$

Assuming $k_{-1} \gg k_2[\text{O}_2]$, the rate law becomes

$$\text{rate} = k_{\text{exp}}[\text{RCo(dmgH)}_2\text{B}][\text{O}_2]$$

Thus the reaction is first order with respect to both the complex and oxygen, as was found in the earlier studies [8]. It is, however, very difficult to choose between this mechanism and a fully concerted mechanism in which the rupture of the Co–C bond and the formation of Co–C and OR bond take place simultaneously. Our results support the recent observations by Gaudemer and Charreton [8].

Decomposition studies

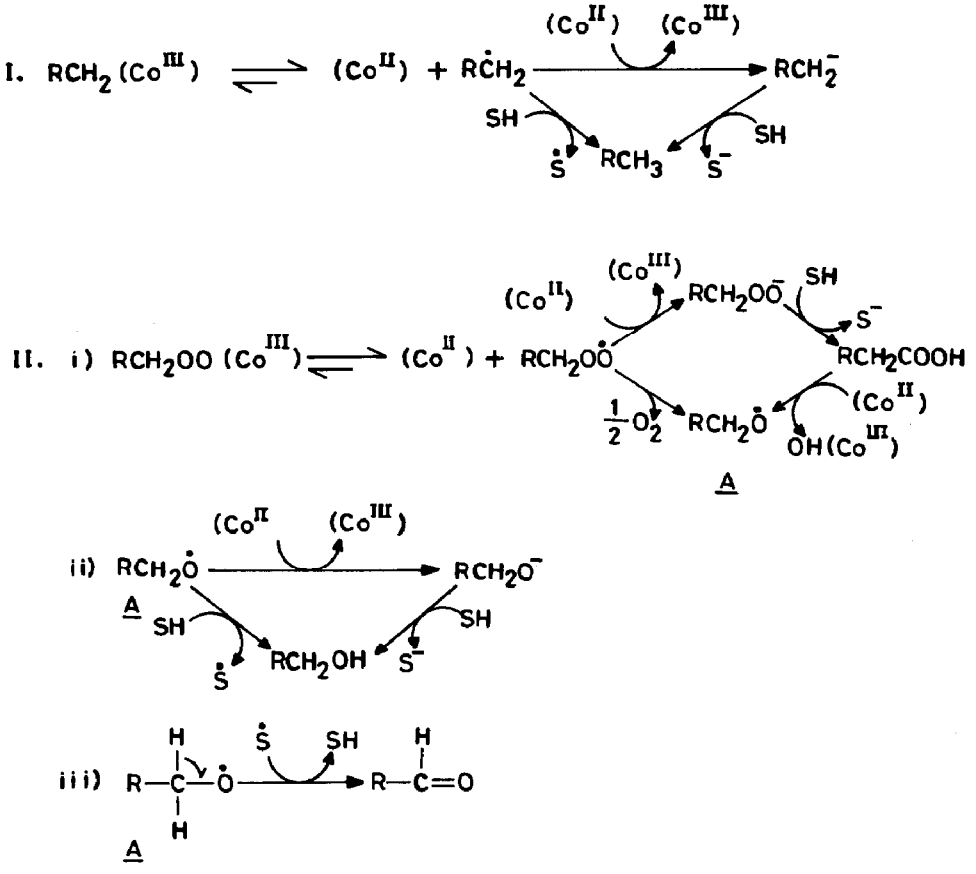
2-Thienylmethyl cobaloxime (**1**) decomposes in refluxing benzene or methanol under nitrogen to give 2-methylthiophene in quantitative yield. The inorganic

Table 4

Organic products [a] from the decomposition of $RCH_2Co^{III}L_2Py$ (**1–14**) and $RCH_2OOCo^{III}L_2Py$ (**1a–14a**)

Compound	Benzene/methanol	Compound	Benzene	Methanol
1 and **8**	2-methyl thiophene	**1a** and **8a**	2-thiopehenecarboxaldehyde	2-thiophene methanol/2-Thiophene carboxaldehyde (95%) (5%)
2 and **9**	3-methyl thiophene	**2a** and **9a**	3-thiophenecarboxaldehyde	3-thiophene methanol/3-thiophene carboxaldehyde (81%) (19%)
3 and **10**	2-methyl furan	**3a** and **10a**	furfural	fufural alcohol/furfural (72%) (28%)
4 and **11**	3-methyl furan	**4a** and **11a**	3-furaldehyde	3-furan methanol/3-furaldehyde (85%) (15%)
5 and **12**	2-methyl benzofuran	**5a** and **12a**	2-benzofuran aldehyde	2-benzofuran methanol/2-benzofuran aldehyde (78%) (22%)
6 and **13**	2-methyl benzothiophene	**6a** and **13a**	2-benzothiophene aldehyde	2-benzothiophene/2-benzothiophene methanol aldehyde (76%) (24%)
7 and **14**	3-methyl benzothiophene	**7a** and **14a**	3-benzothiophene aldehyde	3-benzothiophene/3-benzothiophene methanol aldehyde (82%) (18%)

[a] All products were analysed by GLC on a 10% SE-30 chromo P (85–100 mesh), 2 m column.



Scheme 2

product is a mixture of aquo cobaloxime and hydroxy cobaloxime. Similar reactions of 3-thienylmethyl, furfuryl, 3-furylmethyl, 2-benzofurylmethyl, 2-thianaphthylmethyl and 3-thianaphthyl methyl bis(dimethyl glyoximato)pyridine cobalt(III) complexes (**1**–**7**) and their corresponding bis(cyclohexane dionedioximato)pyridine complexes (**8**–**14**) in refluxing benzene or methanol give the corresponding hydrocarbons RCH_3 (see Table 4). The decomposition of the dioxy adducts (**1a**–**14a**), on the other hand, give rise to aldehydes (RCHO) in benzene, and a mixture of aldehydes (RCHO) and alcohols (RCH_2OH) in methanol. The details of the products formed are summarised in Table 4.

The organic products obtained from the decomposition of the organocobaloximes and their dioxy adducts point to the involvement of R˙ and ROO˙ radicals. In principle, a number of mechanisms can be written for such a decomposition, but we suggest that the pathway shown in Scheme 2 accounts for the products formed. The peroxy radicals and the hydroperoxide have been observed to participate as intermediates in the recently reported oxidations of phenols by molecular oxygen catalysed by cobalt(II) complexes [10].

Experimental

2-Chloromethylthiopene was prepared by the chlorination of thiophene [23]. 3-Bromomethylthiopene was obtained by bromination of 3-methylthiophene with *N*-bromosuccinimide [24]. Furfural alcohol was brominated with PBr_3 in ether, as outlined by Zanetti [25]. Since furfuryl bromide is unstable, its ethereal solution was used in the cobaloxime preparation. 3-Furyl bromide was obtained from propargyl alcohol, paraldehyde, and cobaloxime(I), as described by Tada et al. [26]. Benzofuran and thianaphthene were chloromethylated with HCl and formaldehyde to give 2-chloromethylbenzofuran [27] and 3-chloromethylthianaphthene [28] respectively. Thianaphthene-2-methanol [29] was prepared by the reduction of the corresponding carboxylic acid. The latter was synthesized from 2-mercapto acrylic acid [30]. Thianaphthalene-2-methanol was converted into the chloride by treatment with thionyl chloride.

1,2 Cyclohexane dione dioxime was prepared from 2-bromocyclohexanone and hydroxylamine hydrochloride [31].

Organo bis(dimethylglyoximato)pyridine cobalt(III) complexes were synthesized by reaction of bis(dimethylglyoximato)pyridine cobalt(I) with the appropriate organic halide or tosylate. Cobaloxime(I) was generated in situ by anaerobic alkaline disproportionation of cobaloxime(II) in methanol, as described by Schrauzer [32]. Organobis(cyclohexane dionedioxime)pyridine cobalt(III) complexes were synthesized by the same method except that cyclohexanedione dioxime was used as ligand instead of dimethylglyoxime. 2-Thienylmethyl[bis(dimethyl glyoximato)]-(base)cobalt(III) (base = γ-picoline, morpholine, or piperidine) were synthesized similarly except that the relevant base was used instead of pyridine.

General procedure for oxygen insertion reactions under photochemical conditions

The preparative scale photolyses were carried out in a round bottom flask containing a solution of organocobaloxime (20 mmol in 20 ml CH_2Cl_2) at 0 °C through which dry oxygen gas was passed. The solution was irradiated with two 200 W tungsten lamps placed ca. 5 cm away from the glass apparatus. The reaction was carried to complete conversion of the starting material, and was monitored by TLC on silica gel with ethyl acetate as an eluent. The reaction was complete within 2 h in all cases. At the end of the reaction, the solvent was stripped off at room temperature and the crude product was purified on preparative TLC plate with ethyl acetate as eluent. The yields were almost quantitative in all cases.

Under thermal conditions

The procedure described above was used except that the solution of organocobaloxime in dichloromethane was heated under reflux in the dark. No insertion reaction had occurred in 20 h, but after 50 h, the initial cobaloxime had been consumed (as indicated by TLC), and more than one product was formed. The products were separated on a preparative TLC silica gel plate with a mixture of dichloromethane : acetone (3 : 1, v/v) as eluent.

Decomposition studies

The decomposition experiments were carried out in benzene and in methanol. In a typical experiment, a solution of the organocobaloxime or the dioxycobaloxime

(0.20 mmol in 20 ml of benzene or methanol) was heated to reflux on a steam bath under nitrogen. The reactions carried on until all the starting cobaloxime was consumed, and were monitored by TLC on silica gel with ethyl acetate as the eluent. The reactions were complete within 6–8 h in all cases. The solvent was evaporated and the organic product was extracted with ether. The product was analysed by GLC.

Kinetics of oxygen insertion under photochemical conditions at room temperature (30 °C)

The following general procedure was used. 0.0232 g of 2-thienylmethylcobaloxime (10^{-3} *M*) was dissolved in 50 ml of 95% ethanol. Oxygen was continuously passed at a fixed pressure through the solution at room temperature (30 °C) during it was irradiated with 200W tungsten lamp. The lamp was placed ca. 5 cm from the reaction vessel. The progress of the reaction was monitored by measuring the absorbance at 450 nm at intervals.

In another experiment, a solution of the organocobaloxime (10^{-3} *M*) in 95% ethanol contained in a stoppered spectrophotometric cell was irradiated at room temperature (30 °C) with a 200W tungsten lamp. The progress of the reaction was monitored as above.

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