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Sulphur dioxide insertion into organocobaloximes: a true insertion or a case of radical chain process? *

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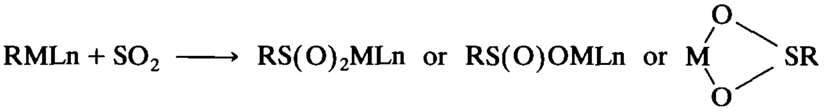
Abstract

Sulphur dioxide gas readily inserts into the Co–C bond of organocobaloximes under photochemical conditions at 0°C, but there is no insertion under thermal conditions. The reactions are not true insertions into the Co–C bond but proceed by a free radical chain process in which the organic and the metal fragment of the inserted product come from different organometallic substrates.

Introduction

There have been numerous reports of sulphur dioxide insertion into σ-bonded organometallic complexes and several reviews of this topic are available [2].



$$RMLn + SO_2 \longrightarrow RS(O)_2MLn \text{ or } RS(O)OMLn \text{ or } M\begin{smallmatrix}O\\ \\ O\end{smallmatrix}SR$$

The metal may be one of many transition or Main Group elements and carbon may be of a wide variety of organic ligands. The reactions have been carried out under thermal and photochemical conditions with or without solvent. Despite the appreciable amount of work on the kinetics, products, and stereochemistries of these reactions, there is no comprehensive picture of the mechanism [3]. This is not surprising since the very ubiquity of the reaction almost certainly implies that there must be a range of mechanisms depending on the metal, and even for a particular metal on the type of organic ligand. The organic group plays an important role especially in sulphur dioxide insertion into the bonded organocobalt(III) complexes; for example, sulphur dioxide inserts readily into the

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alkyl–cobalt bond of a range of primary and secondary alkyl cobalt(III) complexes to give exclusively the corresponding alkane sulphonyl cobalt(III) complexes, whereas the same reaction with alkenyl and alkynyl cobalt(III) complexes gives a mixture of products [3].

Recently, both a chain and non-chain mechanism for the insertion of sulphur dioxide into the C–M bond have been observed [4*].

We report below unambiguous evidence that sulphur dioxide inserts readily into the Co–C bond of benzyl and heteroaromatic methyl cobaloximes [1]. However, the reactions are not true insertions and the products come from an intermolecular free radical process in which organic and metal fragments of the inserted product come from different organometallic substrates.

Results and discussion

Organobis(dimethylglyoximato)pyridine cobalt(III) complexes (**1a–e**) and organobis(cyclohexaneglyoximato)pyridine cobalt(III) complexes (**1f–i**) react under photolytic conditions with sulphur dioxide gas (wet or dry) [5a*] in less than 1.5 h at 0°C to give the corresponding insertion products **2a–i** in nearly quantitative yield. The IR spectra show these to be S-sulphinate complexes. The reactions of **1a–e** are slightly faster (approx. 2 h) (as indicated by TLC analysis) than the corresponding **1f–i** complex (1.5 h). The similar reactions of the corresponding benzo-analogues (**1j–l**) with SO_2 gas are not clean and a side product, insoluble in most of the common organic solvents, is formed in each case along with the desired insertion product. The quantity of the insoluble product is increased by about 20% when wet SO_2 gas is used. Similar observations are made for the reaction of benzyl and para substituted benzyl cobaloximes (**1m–q**) and thiophenoxyl cobaloxime (**1r**) with SO_2 gas. However, the reaction of benzyl cobaloxime (**1m**) with liquid sulphur dioxide in a sealed tube at ambient temperature is much cleaner, and gives **2m** as the sole organometallic product [5b*].

However, a similar reaction with thianaphthylmethyl cobaloxime (**1m**) with liquid sulphur dioxide gives the same mixture of products as obtained from sulphur dioxide gas. The ^1H NMR spectrum of the reaction mixture shows the presence of paramagnetic impurities.

$$\underset{\textbf{(1)}}{RCH_2Co^{III}L_2Py} + \xrightarrow[0°C]{h\nu} \underset{\textbf{(2)}}{RCH_2SO_2Co^{III}L_2Py}$$

RCH_2:

(**a**) 2-Thienylmethyl, L = dmgH
(**b**) 3-Thienylmethyl, L = dmgH
(**c**) Furfuryl, L = dmgH
(**d**) 3-Furylmethyl, L = dmgH
(**e**) 2-Picolyl, L = dmgH
(**f**) 2-Thienylmethyl, L = chgH
(**g**) 3-Thienylmethyl, L = chgH
(**h**) Furfuryl, L = chgH
(**i**) 3-Furylmethyl, L = chgH
(**j**) 2-Benzofurylmethyl, L = dmgH
(**k**) 2-Thianaphthylmethyl, L = dmgH
(**l**) 3-Thianaphthylmethyl, L = dmgH
(**m**) Benzyl, L = dmgH
(**n**) 4-Methylbenzyl, L = dmgH
(**o**) 4-Chlorobenzyl, L = dmgH
(**p**) 4-Cyanobenzyl, L = dmgH
(**q**) 4-Nitrobenzyl, L = dmgH
(**r**) Thiophenoxymethyl, L = dmgH

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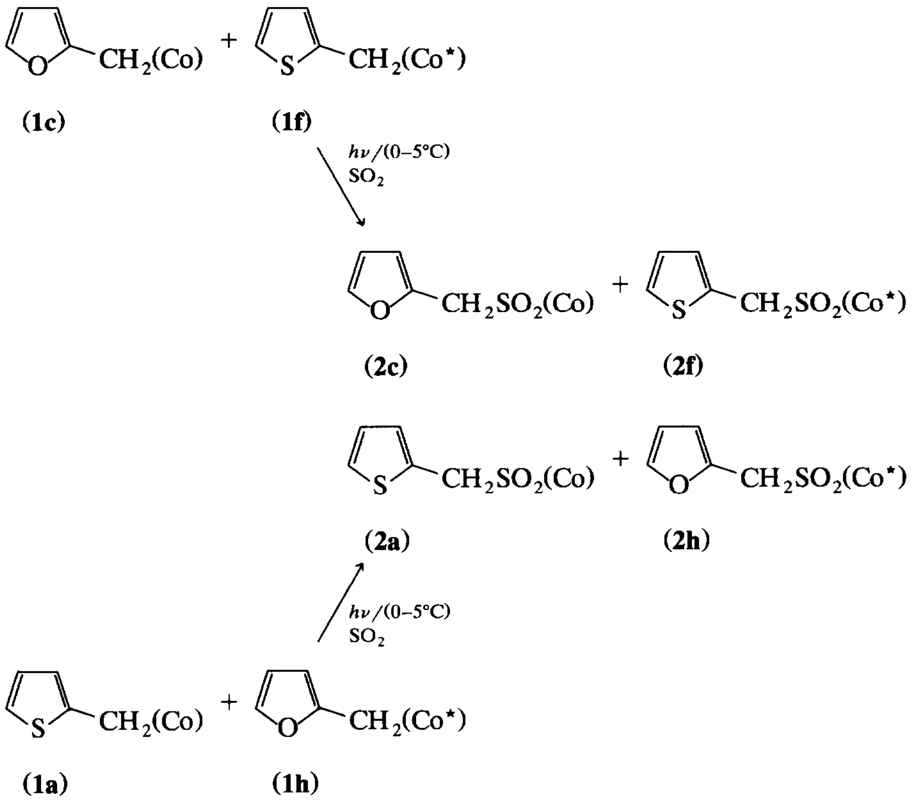
* Reference number with asterisk indicates a note in the list of references.

Table 1

Spectral characteristics of organocobaloximes (**1a–r**) and organo(*S*-sulphinato)cobaloximes (**2a–r**)[a]

Compound no.	^{1}H NMR chemical shift (δ)[b]				UV, λ (nm)[c]
	Aromatic	CH_2	dmgH/chgH	Py	
1	6.65, 7.00	3.00	2.05	7.20, 7.65, 8.50	385, 281, 240
1a	7.15, 7.30	4.15	2.25, 2.38	7.10, 7.70, 8.40	331, 300, 242
1b	6.65, 7.20	2.85	2.00, 2.10	7.30, 7.70, 8.50	359, 277, 239
2b	7.30, 7.40	4.00	2.25, 2.40	7.10, 7.70, 8.40	336, 245, 208
1c	6.00, 7.40	2.40	2.00	7.30, 7.75, 8.60	383, 284, 239
2c	6.20, 7.30	4.30	2.30, 2.40	7.15, 7.50, 8.50	302, 247, 222
1d	6.00, 7.12	2.55	2.00, 2.10	7.15, 7.75, 8.42	348, 286, 238
2d	7.15, 7.30	4.15	2.25, 2.38	7.10, 7.70, 8.40	330, 300, 249
1e	7.00, 8.25	2.85	2.05	7.30, 7.60, 8.55	445, 330, 285
2e	7.50, 7.95, 8.50	4.00	2.32, 2.42	7.50, 7.95, 8.50	302, 251, 208
1f	6.72, 7.05	3.04	1.36–1.80 2.40–2.70	7.25, 7.64, 8.48	365, 315, 247
2f	6.90	4.34	1.46–1.90 2.84–3.14	7.25, 7.74, 8.35	347, 308, 250
1g	6.74, 6.98	2.82	1.60, 1.90–2.10	7.28, 7.70, 8.56	463, 315, 243
2g	7.08–7.50	4.18	1.20–1.90 2.60–3.10	C, 7.80, 8.40	500, 303, 248
1h	6.06	3.54	1.40–1.98 2.55–2.75	7.18, 7.65, 8.50	308, 245
2h	6.28	4.20	1.45–1.92 2.64–3.14	7.25, 7.70, 8.32	303, 247
1i	6.13, 7.16–7.49	2.60	1.30–1.70 2.30–2.90	C, 7.73, 8.59	458, 345, 235
2i	6.43, 7.28–7.71	3.98	1.43–2.05 2.34–3.53	C, 8.00, 8.46	312, 246
1j	6.40, 7.08, 7.18, 7.28, 7.42	2.80	1.28–1.84 2.36–2.58	7.28, 7.77, 8.54	305, 280, 218
2j	6.29, 6.86–7.63	4.56	2.26	C, C, 8.13	325, 287, 280, 244
1k	6.98, 7.20, 7.28 7.62	3.06	1.16–1.86 2.30–2.64	7.31, 7.72, 8.56	303, 253, 228
2k	7.02, 7.08–7.84[d]	4.37	2.40, 2.56	7.29, 7.74, 8.31	338, 249, 226
1l	7.04–7.80	3.04	1.95, 1.85	C, C, 8.46	295, 260, 257, 249, 242
2l	7.07–7.50[d]	4.27	2.15, 2.24	7.13, 7.46, 8.16	362, 292, 241, 217
1m	6.95	2.80	1.90	7.32, 7.73, 8.40	455, 352, 272, 238
2m	7.11–7.52	4.18	2.30	C, 7.78, 8.50	331, 322
1n	6.90[e]	2.90	1.95	7.36, 7.78, 8.52	452, 356, 274, 237
2n	7.10–7.50[f]	4.15	2.35	C, 7.75, 8.50	337, 244, 215
1o	7.20	2.73	2.00	7.30, 7.80, 8.56	455, 353, 270, 240
2o	7.10–7.65	4.10	2.33	C, 7.85, 8.45	331, 244, 218
1p	6.90–7.30	2.71	1.98	7.25, 7.70, 8.50	460, 340, 277, 237
2p	7.13–7.75, 7.89	4.13	2.24	C, C, 8.20	325, 253
1q	6.86–7.54	3.35	2.06	7.72, 8.22, 8.76	445, 350, 300, 235
2q	7.20–7.60 8.00–8.30	4.24	2.35	C, C, 8.45	329, 248
1r	6.98–7.63	3.10	2.00	7.74, 8.10, 8.52	435, 385, 287, 232
2r	7.02–7.97	4.26	2.29	C, C, 8.36	362, 300, 244

[a] All organo(*S*-sulphinato)cobaloximes (**2a–r**) show characteristic IR(KBr) absorption frequencies. ($Co-SO_2$) linkages appear at ν_{sym} (1060–1070) and ν_{asym} (1220–1230) cm^{-1}. [b] In $CDCl_3$, TMS internal standard. [c] In CH_3OH. [d] Obscured. [e] Me resonance appears at 2.04 δ. [f] Me resonance appears at 2.20 δ.



Co = Co(dmgH)$_2$Py   dmgH = dimethylglyoximato (1 −)
Co* = Co(chgh)$_2$Py   dmgH = cyclohexaneglyoximato (1 −)

Scheme 1.

When an equimolar mixture of **1c** and **1f** is treated with SO_2 gas under the photolytic conditions, along with the expected products, **2c** and **2f**, two additional products, **2a** and **2h**, are present, as shown by the ^{1}H NMR spectrum. Similar reaction of a mixture of **1a** and **1h** with SO_2 gas gives a mixture of four products **2a**, **2c**, **2f** and **2h**. All attempts to separate these insertion products by chromatography or partial crystallisation failed (Scheme 1).

The following conclusions were reached from the various experiments.

(a) No insertion product is formed at 0°C without irradiation.
(b) All the reactions show a concentration-dependent induction period. However, after the induction period the reaction proceeds to completion without any further irradiation.
(c) The reaction is inhibited by radical traps such as galvinoxyl and accelerated by added cobaloxime(II).
(d) No exchange of **1c** and **1f** into **1a** and **1h** and *vice versa* occurs under the reaction conditions in the absence of sulphur dioxide.
(e) Once the insertion product is formed it is very stable and no rearrangement of any kind takes place; for example, there is no rearrangement of **2c** and **2f** to **2a** and **2h**, or *vice versa*, under the reaction conditions.

(f) No insertion product is formed under thermal condition (refluxing dichloromethane) in the dark, and the starting material is recovered after a few hours.

Spectra and structure

The $\nu(SO_2)$ bands in the infrared spectra of **2a**–**r** appear at 1060–1070 cm^{-1} and 1220–1230 cm^{-1}, a range predicted for S-bonded sulphinate groups in many known organocobaloxime complexes [3].

The main points of interest in the ^1H NMR spectra of **2a**–**r** are the effect of the intervening SO_2 group on the protons of the RCH_2 group and the effect of the RCH_2SO_2 group on the planar dimethyl glyoxime ligand protons. The downfield shift for the RCH_2 group and the CH_3 resonance of the equatorial ligand are in accordance with previous reports [3].

All the reactions described above are free radical in nature. The radical nature of these reactions is apparent from the observation that the rates of the reactions are variable and subject to induction periods. The cleavage of the Co–C bond is a key feature of these substrates, and it is well established that the organocobaloximes [6] undergo unimolecular homolysis under thermal and photochemical conditions. The cleavage of the Co–C bond in organocobaloximes takes place very readily even on irradiation at wavelengths greater than 360 nm [6]; this is consistent with the low bond energy of the Co–C bond, which is between 17 and 25 kcal/mol in such substrates. Thus tungsten lamps and glass apparatus can be used in preparative photolysis experiments. Cobaloxime(II) has been shown to be a good leaving group in many known homolytic displacement reactions [7].

Further indirect support for the radical nature of these reactions come from the earlier studies of SO_2 insertions into hexenyl and butenyl cobaloximes in which one of the products obtained is a cyclised species. The product is formed as a consequence of the ability of the hexenyl radical to undergo cyclisation reactions [3c]. Cyclisation without prior dissociation of the Co–C bond is ruled out.

From the nature of products obtained, the influence of galvinoxyl and adventitious cobaloxime(II) and observations on homolytic displacements at carbon in such cobaloximes, we suggest that the reactions are not true insertions and that the experimental observations can be accounted for in terms of the radical chain mechanism shown in Scheme 2. The concerted mechanism, involving attack of sulphur dioxide on the metal and the organic group, is ruled out by the experimental observations.

The product RSO_2Co^{III} may arise by two independent routes, A and B, involving the propagation steps 2, 3, 4 and 5. From our earlier studies it is known that reaction 5 is a key step in many homolytic displacement reactions in organocobaloximes. Thus any RSO_2 radical formed during the reaction must attack the R group of the organocobaloxime. It is therefore rather unlikely that RSO_2Co^{III} arises by route B [8*], and so the preferred route for the formation of RSO_2Co^{III} must be route A [9*]. There is a precedent for reaction 2 in the direct reaction of SO_2 with Co^{II} complexes such as $Co(CN)_5^{-3}$ and $Co(dmgH)_2Py$. The former gives the well characterized anion $\{[Co(CN)_5]_2SO_2\}^{6-}$, apparently via reactions 2 and 6 [10], but the corresponding complex $(Co(dmgH)_2Py)_2SO_2$ is less well characterized. It is significant that the latter complex is also formed as a

Initiation:

$$\mathrm{RCH_2Co^{III}} \xrightarrow{h\nu} \mathrm{R\dot{C}H_2 + Co^{II}} \qquad (1)$$

Propagation:

$$\text{Route A:} \quad \mathrm{Co^{II} + SO_2} \longrightarrow \mathrm{Co^{II}SO_2} \qquad (2)$$

$$\mathrm{Co^{II}SO_2 + RCH_2Co^{III}} \longrightarrow \mathrm{Co^{III}SO_2CH_2R + Co^{II}} \qquad (3)$$

$$\text{Route B:} \quad \mathrm{R\dot{C}H_2 + SO_2} \longrightarrow \mathrm{RCH_2\dot{S}O_2} \qquad (4)$$

$$\mathrm{RCH_2\dot{S}O_2 + RCH_2Co^{III}} \longrightarrow \mathrm{RCH_2SO_2Co^{III} + R\dot{C}H_2} \qquad (5)$$

Termination:

$$\mathrm{Co^{II}SO_2 + Co^{II}} \longrightarrow \mathrm{Co^{III}SO_2Co^{III}} \qquad (6)$$

$$\mathrm{RCH_2\dot{S}O_2 + Co^{II}} \longrightarrow \mathrm{RCH_2SO_2Co^{III}} \qquad (7)$$

$\mathrm{Co = Co(dmgH)_2Py}$ or $\mathrm{Co(chgH)_2Py}$

Scheme 2.

by-product ($< 10\%$) in the reaction of SO_2 with a mixture of benzylcobaloximes and *p*-bromobenzylcobaloxime [4a].

The above mechanism is by no means general for SO_2 insertions into organocobaloximes, but has also been observed for organoiron complexes under extreme conditions [4a]. For example, in the reaction of SO_2 with a mixture of **A** and **B**, about 5–15% [4b*] of the inserted cross product $\mathrm{PhCH_2SO_2Co^{III}(dmgH)_2Py}$ is also formed, implying attack of the $\mathrm{Py(dmgH)_2Co \cdot SO_2}$ radical on the organoiron complex.

$$\underset{\textbf{(A)}}{\mathrm{PhCH_2Fe(CO)_2(cp)}} + \underset{\textbf{(B)}}{\mathrm{4\text{-}BrC_6H_4CH_2Co^{III}(dmgH)_2Py}} \longrightarrow \underset{5\text{–}15\%}{\mathrm{PhCH_2SO_2Co^{III}(dmgH)_2Py}}$$

Interestingly, no cross-insertion products are formed in the reaction of SO_2 with a mixture of (**A**) and organomolybdenum complexes [4a]. Jacobsen and Wojcicki [4c] have observed a similar absence of cross-products in the reaction of SO_2 with mixtures of **A** and other organomolybdenum complexes.

In view of Jacobson and Wojcicki's results [11], it is possible that the mechanism of SO_2 insertion in liquid SO_2 may be different from that in organic solvents, since some differences are found in the reaction order as R is varied. However, it is very difficult to extend the argument to the present studies since we do not know the precise change in rates in liquid SO_2 or in the solvent (CH_2Cl_2). However, it is noteworthy that the reaction is much cleaner in liquid SO_2 in the case of benzylcobaloximes, which gives solely the insertion product, whereas a similar reaction with SO_2 gas gives a side product as mentioned above. However, in the case of benzo-analogues, identical products are obtained from SO_2 gas and liquid SO_2.

The results indicate clearly that the free radical chain mechanism is dominant in the organocobaloximes and may operate in other systems, such as those involving organoiron, organomolybdenum, and similar complexes, when there is adequate initiation and when the concentrations are extremely high and the stability of the displaced metal is such that the propagation step 3 is favoured.

In view of our results it seems that the lack of reaction of $MeCo^{III}(dmgH)_2Py$ with pure dry sulphur dioxide reported previously [12], may have been a result of the absence of a radical initiator rather than, as previously suggested, the absence of water.

Interestingly, oxygen insertions into the same complexes are free radical but non-chain in nature [13].

Experimental

All the organocobaloximes and the organic precursors were synthesized by the procedures outlined in our earlier paper [13a]. 2-Picolyl bromide was prepared by a four-step route from 2-picoline [14]. Tosylation of 2-picolylalcohol was carried out as described by Klamman *et al.* [15]. 2-Picolyl bromide on treatment with cobaloxime (**1**) under alkaline conditions gave only a 10% yield of the desired product whereas the tosylate gives a 60% yield. Cobaloxime(I) was synthesized either by sodium borohydride reduction of chlorocobaloxime(III) or by alkaline disproportionation of cobaloxime(II) [16].

General procedure for sulphur dioxide insertion reaction

A solution of 2-thienylmethylcobaloxime (20 mmol) in 20 ml of CH_2Cl_2 was purged with a stream of dry nitrogen gas to remove all traces of oxygen, then irradiated with 2 × 200 W tungsten lamps placed at about 10–20 cm from the water-cooled Pyrex glass apparatus. The temperature was maintained at 0°C by use of a Julabo refrigerator circulator, and sulphur dioxide gas was bubbled through the solution under a positive pressure of nitrogen. The reaction was carried on until all of the starting cobaloximes had disappeared, and was monitored by TLC on silica gel with ethyl acetate as the eluent. After completion (approx. 1 h) the solvent was removed and the product purified on a preparative silica gel TLC plate with ethyl acetate as solvent.

Reaction of sulphur dioxide with a mixture of two cobaloximes

In a typical experiment, 2-thienylmethyl bis(dimethylglyoximato)pyridine cobalt(III) (**1a**) (0.2 mmol) and furfuryl bis(cyclohexane glyoximato)pyridine cobalt(III) (**1h**) (0.2 mmol) were dissolved in dichloromethane (50 ml) and the reaction was carried out as described above. After work-up, the ^1H NMR spectrum of the product mixture showed the presence of four compounds, which were identified by comparison of their spectra with those of authentic samples. All attempts to separate the four products by chromatography or partial crystallisation failed.

Acknowledgement

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