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SULPHUR DIOXIDE INSERTION INTO ORGANOCOBALOXIMES: A TRUE INSERTION OR A CASE OF RADICAL CHAIN PROCESS!

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Summary. The insertion of sulphur dioxide into Co-C bond of organocobaloximes, $RCo^{III}(dmgH)_2Py$ (R = 2- and 3-thienyl methyl, furfuryl and 3-furyl) occurs readily under photochemical stimulations at 0 °C, but there is no insertion under thermal conditions. The reactions are not true insertions but occur by a radical chain process.

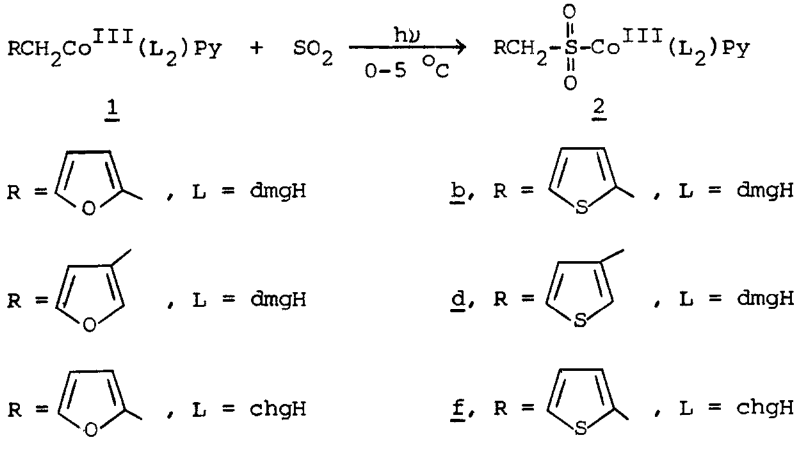
Sulphur dioxide insertion into a metal-carbon bond takes place with a wide variety of σ bonded organometallic complexes of both main groups and transition elements.

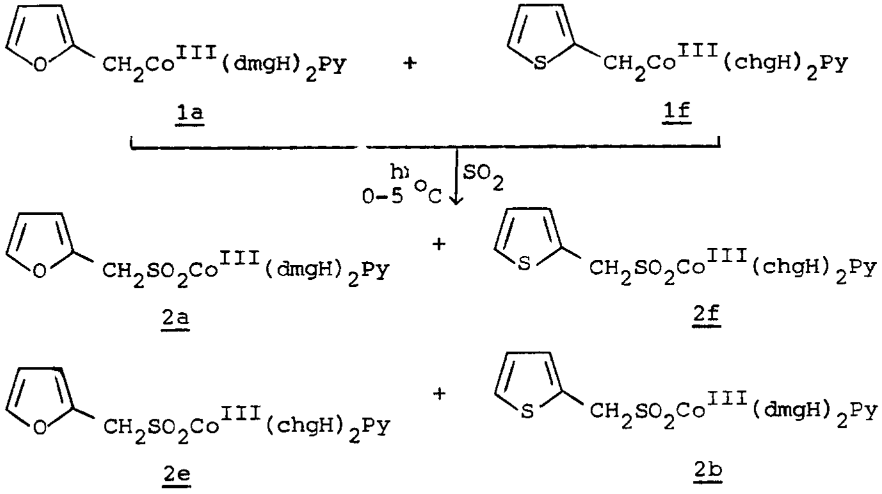
$$RML_n + SO_2 \longrightarrow RS(O)_2ML_n \text{ and/or } RS(O)OML_n$$

Many excellent reviews have been published on the subject.[1] Despite a great deal of work on the kinetics and stereochemistry of these reactions no unified mechanism has emerged so far. This is not surprising since the very ubiquity of the reaction almost certainly demands a range of different mechanisms appropriate to each metal and even for a particular metal, to each type of organic ligand. Recently, both a chain and non-chain mechanism for the insertion of SO_2 in C-M bond have been pointed out.[2]

In this paper we present an unambiguous experimental evidence that SO_2 insertion reactions in thienyl methyl, furyl and furfuryl cobaloximes are not true insertions into Co-C bond and the products result as a consequence of the intermolecular process in which the organic and the metal fragments of the inserted product do not arise from the same organometallic substrate.

Furfuryl cobaloxime 1a reacts under photolytic conditions with SO_2 gas in less than one hour at 0-5 °C to give the corresponding inserted product 2a in nearly quantitative yield.[3] Similar reactions of 1b, 1c and 1d under identical conditions give the corresponding inserted products 2b, 2c and 2d, respectively. On the other hand, 1e and 1f require similar conditions but slightly longer times (1.5 hr) to form 2e and 2f, respectively. These reactions form one of the fastest insertion reactions studied so far in cobaloximes. No insertion product is formed under thermal conditions in any case. However, when an equimolar mixture of 1a and 1f is reacted with SO_2 gas under the above conditions, besides the expected products 2a and 2f, two additional products 2e and 2b are observed in the ^1H NMR spectrum.[4]





Furthermore, the following information is obtained from independent experiments:

1. No exchange of 1a and 1f into 1b and 1e occurs under the reaction conditions in the absence of SO_2.
2. Once the products 2a and 2f are formed, they are very stable and no rearrangement of any kind takes place.
3. No insertion of SO_2 into 1b occurs without irradiation.
4. All reactions show concentration dependent induction time, however, once the induction time is over, the reaction proceeds to completion without irradiation.

5. The reactions are significantly inhibited by radical inhibitor like galvinoxyl and becomes faster with adventitious cobaloxime(II).

All the reactions described in this paper are free radical in nature. The cleavage of Co-C bond is the key feature of these substrates and it is well established that the organocobaloximes undergo unimolecular homolysis under thermal and photochemical conditions. This is consistent with the low bond energy of Co-C bond which falls between 17-25 kcal mole^{-1} in such substrates.[5] Cobaloxime(II) has been shown to be a good leaving group in many known homolytic displacement reactions.[6]

From the nature of the products obtained, influence of galvinoxyl and adventitious cobaloxime(II) and based on our recent work on homolytic displacements at carbon we propose that the reactions are not true insertions and the experimental observations can be explained by the following radical chain mechanism.

Initiation: $RCo^{III} \overset{h\nu}{\rightleftharpoons} \dot{R} + Co^{II}$ .. (1)

Propagation - Route A : $Co^{II} + SO_2 \longrightarrow Co^{II}SO_2$ .. (2)

$Co^{II}SO_2 + RCo^{III} \longrightarrow RSO_2Co^{III} + Co^{II}$ .. (3)

Route B : $\dot{R} + SO_2 \longrightarrow R\dot{S}O_2$ .. (4)

$R\dot{S}O_2 + RCo^{III} \longrightarrow RSO_2Co^{III} + \dot{R}$ .. (5)

Termination: $Co^{II}SO_2 + Co^{II} \longrightarrow Co^{III}SO_2Co^{III}$ .. (6)

$R\dot{S}O_2 + Co^{II} \longrightarrow RSO_2Co^{III}$ .. (7)

RCo^{III} = $RCo^{III}(dmgH)_2Py$ or $RCo^{III}(chgH)_2Py$
dmgH = dimethyl glyoxime monoanion
chgH = cyclohexane glyoxime monoanion.

The product RSO_2Co^{III} may arise by two independent routes A and B involving the propagation steps (2), (3) and (4), (5), respectively. It is well established from our recent work that $R\dot{S}O_2$ (R = alkyl or aryl) exclusively attacks the carbon centre and not the metal and forms RSO_2R, it is quite unlikely that RSO_2-Co^{III} may arise by route B. Therefore, the preferred route responsible for the formation of RSO_2Co^{III} may be route A.[7] Although there is a good precedent for the route A in literature, species like $Py(dmgH)_2Co$-SO_2-$Co(dmgH)_2Py$ which are known to form as side product in certain SO_2 insertion reactions are not well characterised.[2] To confirm the validity of attack of $Co^{II}SO_2$ on carbon centre in $RCo^{III}(dmgH)_2Py$, studies are underway in our laboratory.

Interestingly, oxygen insertion into the same complexes are free radical but non-chain in nature and the insertion occurs via a base on process.[8]

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3. In a typical expt. a dilute soln. of organocobaloxime (0.2 mmol) in 20 ml CH_2Cl_2, is used. All the compounds are characterized by their ^1H NMR, IR spectra and their elemental analysis. Only S-sulphinate derivatives are formed in all cases.
4. Efforts to separate these four products by chromatography failed but the products were identified and confirmed by comparison with the authentic samples obtained from independent experiments.
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