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STUDIES ON THE INTERACTION OF PEROXY RADICALS WITH TRANSITION METALS COMPLEXES

I. EFFECT OF 2-CYANO-2-PROPYL AND 2-CYANO-2-PROPYL PEROXY RADICALS ON COBALOXIMES

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Summary

Reactions of $CH_3Co(DH)_2py$ (**1**) and $[Co(DH)_2py]_2$ (**2**) with $(CH_3)_2(CN)C^{\cdot}$ ($r^{\cdot}$) and $(CH_3)_2(CN)COO^{\cdot}$ ($rO_2^{\cdot}$) radicals were investigated. At 60°C, reaction of $r^{\cdot}$ with (**1**) results in non-homogeneous ligand decomposition, whereas for **2**, complex $(CH_3)_2CNCCo(DH)_2py$ (**6**) and a precipitate are formed. Ligand decomposition also took place at 60°C when the reaction of $rO_2^{\cdot}$ radicals with **1** and **2** was investigated. However, the same reaction with $rO_2^{\cdot}$ radicals at -10°C, yielded two complexes, $CH_3OOCo(DH)_2py$ (**3**) and $Co(DH)_2py$ (**4**) with **1**, and complex **6** for the reaction of $rO_2^{\cdot}$ with **2**.

Introduction

The effect of transition metal complexes on the liquid-phase oxidation of hydrocarbons has been widely studied [1]. It has been established that these complexes participate in nearly all steps of the oxidation process.

As an overall effect catalysis by these complexes is observed, although under certain experimental conditions inhibition can occur.

Such a phenomenon was described by Betts and Uri [2] and also by Knorre et al. [3] who defined it as the dual function of transition metal complexes. Interestingly, in the same system, it has been observed that by simply varying the given conditions, catalysis turns into inhibition or vice versa [4].

Though various interpretations are published in the literature in order to explain this phenomenon, the chemical aspects have not been satisfactorily established.

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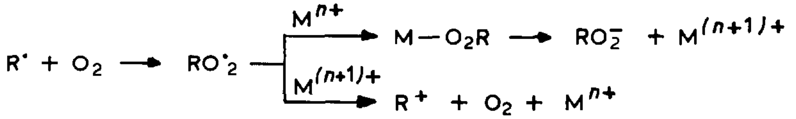
It may be assumed that the dual function of the catalyst is a result of its simultaneous interaction with the stable intermediates of the oxidation and with chain-carrier radicals. Depending on the relative contribution of these interactions one obtains either overall catalysis or overall inhibition, the dominant reaction masking the counter-effect which is, however, always present in the system.

Reactions of metal complexes with O_2 [2,5] and stable intermediates of hydrocarbon oxidation e.g. hydroperoxides [6–8] and alcohols [9–11] have been investigated.

Reactions between metal complexes and radicals have so far been investigated, though, mainly from a kinetic point of view [12–14,16]; while the chemical approach has been largely neglected.

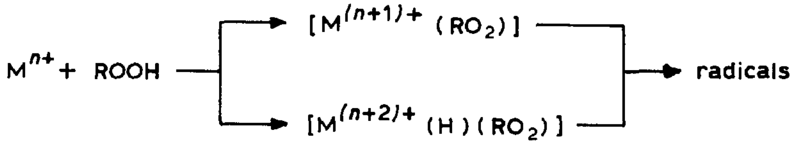
Peroxy radicals are essentially formed in the propagation steps of the oxidation forming stable $M{-}O_2R$ bonds, followed by their decomposition into non-radical products (reaction 1).



(1)

where M is the metal ion.

However, similar bonds can also be formed during the catalytic decomposition of hydroperoxide molecules (reaction 2).



(2)

According to the literature, stable complexes of peroxy radicals with Co [8,15–17], Mn [15], Ir [18], Pd [19], V [15,20] and Mo [21] complexes have been obtained after their respective reactions with hydroperoxides in dry non-polar solvents and in an oxygen-free atmosphere.

Fontaine et al. [22] have observed that photochemical insertion of oxygen into the metal–carbon bond of cobalt alkyl complexes results in the coordination of peroxy radicals to the complex (reaction 3).

$$RCo(DH)_2py + O_2 \xrightarrow{h\nu} RO_2Co(DH)_2py \qquad (3)$$

where DH denotes the $HON{=}C(CH_3)C(CH_3){=}NO^{-}$, anion of dimethylglyoxime and py = pyridine

Here we deal with the direct interaction of peroxy-radicals generated during the decomposition of an azo-initiator [azo-bis(isobutyro nitrile) = AIBN] with dimethylglyoxime complexes of cobalt.

Experimental

Materials

Methyl(pyridine)bis(dimethylglyoximato)cobalt, $CH_3Co(DH)_2py$ (**1**) and (pyridine)bis(dimethylglyoximato)cobalt, $[Co(DH)_2py]_2$ (**2**) were synthesized according to the method by Schrauzer [23]. Their elemental analyses, NMR, IR and electronic spectra were satisfactory. AIBN was dissolved in acetone and precipitated with water. The solvents; CCl_4, $CHCl_3$, C_6H_5Cl, C_6H_6 were dried and distilled before use.

Experimental procedure

Reactions were carried out both thermally (at 50–80°C) and photochemically (at −10°C). An HBO200 mercury lamp was used as the light source. In the starting mixture, the cobalt complex:AIBN molar ratio was 1:2. When 2-cyano-2-propyl radicals were studied instead of peroxy radicals, the decomposition of AIBN was carried out under argon at 60°C. The precipitates formed during the reactions were filtered off and washed with the solvent and then with diethyl ether.

If no precipitation occurred during the reaction, the solvent was evaporated off in a vacuum evaporator and the residue washed carefully with diethyl ether. The course of the reaction was followed by monitoring the electronic spectra of the reaction mixture, as well as by NMR and IR spectroscopy. Vibrational spectra were recorded on a Nicolet FT-IR, the ^1H NMR spectra on a Varian XL-100 and the electronic spectra on a Specord UV-VIS apparatus.

Results and discussion

It is known that under certain conditions alkylcobaloximes can be converted into complexes containing the alkylperoxy radical [16,21,24] (reactions 3 and 4).

$$RCo(DH)_2py \xrightarrow{R'OOH} R'OOCo(DH)_2py \qquad (4)$$

R = alkyl   R′ = cumyl, t-butyl

Under favorable conditions complex **2** can also add radicals [25] (reaction 5).

$$[Co(DH)_2py]_2 \xrightarrow{R^{\cdot}} RCo(DH)_2py \qquad (5)$$

Our aim was to determine what the products were of the reaction of cobaloximes **1** and **2** with the radicals formed during the decomposition of AIBN under argon and oxygen. The thermal decomposition of AIBN follows simple first-order kinetics at about the same rate in a variety of solvents yielding 2-cyano-2-propyl ($r^{\cdot} = (CH_3)_2(CN)C^{\cdot}$) or 2-cyano-2-propyl peroxy ($rO_2^{\cdot}$) radicals in argon or oxygen, respectively. The rate constant of decomposition of AIBN at 50°C in CCl_4 is $2.5 \times 10^{-6}\ s^{-1}$ [26]. AIBN also decomposes photochemically during irradiation with visible light [27].

Reactions of $CH_3Co(DH)_2py$

Reaction of $CH_3Co(DH)_2py$ in the absence of AIBN. Compound **1** is rather stable in CCl_4. Both under argon and oxygen, after a couple of hours only trace

TABLE 1

^{1}H CHEMICAL SHIFTS (ppm) OF THE COBALT COMPLEXES WITH DIMETHYLGLYOXIME IN $CDCl_3$ ^{a}

Compound	CH_3 (R)	CH_3 (DH)	Pyridine		
			H_α	H_β	H_γ
(1) $CH_3Co(DH)_2py$	0.82	2.09	8.40	7.30	7.70
(2) $[Co(DH)_2py]_2$		2.17	8.63	7.22	7.60
(3) $CH_3OOCo(DH)_2py$	3.22	2.31	8.27	7.22	7.70
(4) $Co(DH)_2py$		2.36	8.29	7.25	7.69
(5) $ClCo(DH)_2py$		2.41	8.27	7.22	7.70
(6) $(CH_3)_2(CN)CCo)DH)_2py$	1.27	2.35	8.63	7.28	7.62
(7) $(CH_3)_2(CN)COOCo(DH)_2py$	1.30	2.33	8.32	7.23	7.66

^{a} TMS was used as internal standard.

amounts of products of the type $Co(DH)_2py$ (**4**) were obtained at 60°C, revealed by NMR measurements (see Table 1). The Cl in compound **5** is derived from the solvent.

Reaction of $CH_3Co(DH)_2py$ with $r^\cdot$ radicals. Destruction of dimethylglyoxime by the $r^\cdot$ radicals was observed under argon at 60°C. The green precipitate formed after reaction of **1** with AIBN contained no dimethylglyoxime, as determined from the NMR and IR spectra.

Reaction of $CH_3Co(DH)_2py$ with $rO_2^\cdot$ radicals. Interaction of **1** with $rO_2^\cdot$ generated thermally in either a CCl_4, C_6H_5Cl or C_6H_6 solution, resulted in the immediate formation of a brown precipitate with properties very different from those of the starting material.

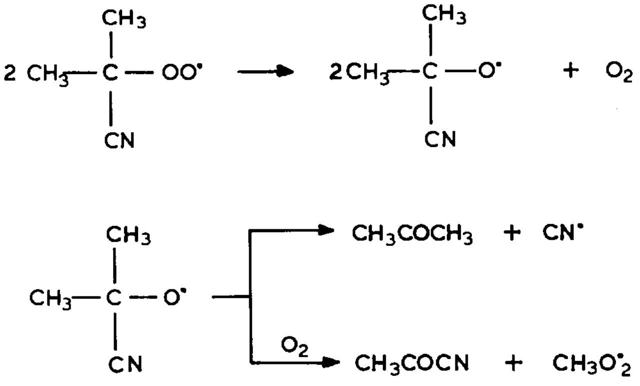
NMR and IR measurements revealed that the reaction products did not contain the metal coordinated methyl group, since no signal was observed at 0.82 ppm in the NMR spectrum nor were the bands at 2900 and 2800 cm^{-1}, $\nu(CH, CH_3)$, present in the IR spectrum.

The IR spectrum of the thermal reaction products of compound **1** showed a broadenining and decrease in intensity the band at 1560 cm^{-1} $\nu(C{=}N, DH)$. This indicated the destruction of the dimethylglyoxime anion and was most probably due to the removal of one of the bridging hydrogens from the chelating system for the production of the DH^{2-} dianion.

New bands simultaneously appeared at 1273, 1318, 1656 and 3400 cm^{-1}, as a result of the coordination of the decomposition products of AIBN (containing C=O and OH groups) to cobalt.

In the spectrum of the reaction products of compound **1**, the band at 2155 cm^{-1} was (tentatively) assigned to the CN group, coordinated to cobalt, and formed during the thermal decomposition of AIBN. In the case of $CNCo(DH)_2CN$ this band appears at 2130 cm^{-1} [28]. Cyanide is known to be a tightly-bound ligand in cobaloximes; its affinity is more than 200 times greater than that of pyridine [29].

The course of reaction of **1** or **2** with the $rO_2^\cdot$ radicals generated photochemically at $T \leqslant -10°C$ is different. In the case of compound **1**, CH_3 was not replaced by $rO_2^\cdot$. Instead, two different products were observed in a 1:1 ratio. One, $CH_3OOCo(DH)_2py$ (**3**), was formed by insertion of oxygen into the carbon–cobalt bond, while formation of the other, $Co(DH)_2py$ (**4**), was due to the photolysis of **1**.



SCHEME 1

Another possibility for the formation of 3 is the substitution of CH_3 group by the $CH_3O_2^{\cdot}$ radical formed in the following reaction pathway, see Scheme 1.

Although this pathway seems reasonable, products containing the $rO_2^{\cdot}$–Co group could not be identified. The fact that there is no competition between $CH_3O_2^{\cdot}$ and $rO_2^{\cdot}$ radicals rules out attack by the free peroxy radical (radical chain mechanism) which leaves only the radical-cage mechanism for the formation of compound 3. In CCl_4 solutions, $ClCo(DH)_2py$ (5) is also formed as the product of radical interaction with CCl_4 [30]. Compounds 3, 4 and 5 were identified from their NMR spectra (Table 1).

Properties of compound 3 are identical to those reported by Giannotti [24], except for the IR spectrum, where the band at 1000 cm^{-1} corresponding to O–O bond vibration in the peroxy group, is not present. However, it is more likely that this band should be located at 865 cm^{-1}, i.e. in the frequency range where the O–O group vibrations are observed in peroxy complexes of iridium [18] and palladium [18], as well as in hydroperoxides [31]. The fact that the $rO_2^{\cdot}$ radicals have no influence on the formation of complex 3 suggests a radical-cage mechanism for its formation.

Reactions of $[Co(DH)_2py]_2$

Reaction of $[Co(DH)_2py]_2$ with $r^{\cdot}$ radicals. A new product, 6, was observed when the reaction was carried out under argon, at 60 °C, and was characterized by a signal typical for the glyoximic methyl group of Co^{III} compounds, NMR signals of which appeared at 2.1 ppm. From the signal at 1.27 ppm the new substituent is probably $(CH_3)_2(CN)C^{\cdot}$.

Reaction of $[Co(DH)_2py]_2$ with $rO_2^{\cdot}$ radicals. In the thermal reaction compound 2 behaves in the same way as compound 1.

The photochemical reaction of compound 2 with AIBN under oxygen at $T \leqslant -10\,°C$, in C_6H_5Cl, yielded the compound $(CH_3)_2(CN)COOCo(DH)_2py$ (7) (reaction 7).

$$Co(DH)_2py + rO_2^{\cdot} \xrightarrow[C_6H_5Cl]{h\nu,\,-10\,°C} rO_2Co(DH)_2py \qquad (7)$$

$Co(DH)_2py$ is the monomeric form of complex **2** and is formed from the dimer under the influence of light.

Compound **7** was identified by NMR spectroscopy (see Table 1). Singlets of the methyl groups of dimethylglyoxime and of the methyl groups of the peroxy radicals were observed at 2.33 ppm and at 1.33 ppm, respectively. In AIBN the latter signal is observed at 1.73 ppm while in 2-cyano-2-propyl hydroperoxide it is present at 1.62 ppm. A similar shift in signal caused by coordination with cobalt is observed for the following compounds: $Ph(Me)_2COOH$ (1.55 ppm) [19] and $Ph(Me)_2COO$-$Co(DH)_2py$ (1.26 ppm) [24]. The latter compound was synthesized and characterized by Giannotti et al. [24].

The IR spectrum of compound **7** shows two weak bands at 885 and 525 cm^{-1} which could be assigned to ν(O–O) and ν(Co–O), respectively.

The electronic spectrum of compound **7** is similar to those obtained for cobalt compounds, synthesized by Giannotti et al. [24], having bands at 28 300, 32 300 and 40 000 cm^{-1}.

Attempts, however, to synthesize compound **7** from $Co(DH)_2py$, obtained from the photolysis of complex **1** failed. This indicates that the mechanism of the formation of compound **7** requires prior formation of an adduct, e.g. $Co(DH)_2pyO_2$, which can be obtained from compound **2**, in the presence of oxygen at low temperatures [32].

Conclusions

Metal alkylperoxy complexes, formed by the interaction of a metal complex with peroxy radicals can be synthesized only at low temperatures. At higher temperatures such complexes undergo decomposition to yield non-homogeneous products.

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