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Cleavage Reactions of Alkylcobaloximes with Anhydrous Hydrogen Chloride

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The compounds $RCo(DH)_2py$ (R = alkyl; DH = dimethylglyoximato anion) are cleaved by anhydrous HCl in chlorinated solvents to give RH (R = Me, Et, isopropyl, neopentyl, cyclohexyl), probably via an S_E2 process. When R = benzyl, homolysis of the cobalt–carbon bond becomes the predominant reaction, yielding bibenzyl.

Introduction

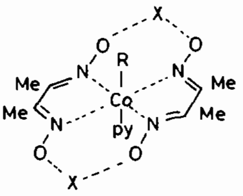
Although mechanisms of electrophilic cleavage reactions of alkyltransition metal compounds have elicited considerable interest in recent years [1], acid cleavage reactions, which normally produce hydrocarbons (equation 1), have been little studied.

$$L_nM{-}R + HX \rightarrow L_nMX + HR \qquad (1)$$

(R = alkyl, aryl; L = other ligands; X = anion)

To date, kinetic and stereochemical data for reactions as in equation (1) are available only for compounds of the type η^5-$C_5H_5Fe(CO)_2R$ [2, 3]. It has been shown that cleavage of the iron–carbon bonds probably proceeds via protonation of the iron to form the species $[C_5H_5Fe(CO)_2(R)H]^+$, followed by reductive elimination of RH with retention of configuration.

We are currently extending our earlier studies [3] to an investigation of acid cleavage reactions of alkylcobaloxime compounds, $RCo(DH)_2py$ (*I*: R = alkyl, DH = dimethylglyoximato anion; py = pyridine).



I

(a) X = H

(b) X = D

Cleavage reactions of alkylcobaloximes with electrophilic reagents other than the proton have been recently reviewed [1]. In addition, it has been reported that alkylcobaloximes readily produce hydrocarbons, RH, on photolysis and thermolysis, both via homolysis of the cobalt–carbon bond [4]. Similar products are formed on treatment with aqueous hydroxide [5, 6] and treatment with hydrogen [7]. A recent report concerning the trifluoroacetic acid cleavage reactions of alkylcobaloximes [8] prompts publication of our own results on the hydrogen chloride cleavage reactions of these compounds.

Experimental

The compounds $RCo(DH)_2py$ (*Ia*: R = Me [5], Et [5], iso-Pr [5], neopentyl [9], cyclohexyl [10], 4-methylcyclohexyl [11], benzyl [12]) have all been reported previously. The labelled analogues, *Ib*, were prepared by washing a chloroform solution of *Ia* with D_2O in the dark until the hydroxyl resonance in the ^1H NMR spectrum ($\delta \approx 18$) had disappeared. Absence of the broad band at ~1740 cm^{-1} in the IR spectrum, attributable to the O–H—O moiety [5], confirmed the completeness of the exchange reaction. The compounds $Co(DH)(DH_2)Cl_2$ [13] and K_2CoCl_4 [14] were prepared as in the literature.

Cleavage reactions with anhydrous HCl or DCl were performed in purified methylene chloride, chloroform-d_1 or *o*-dichlorobenzene in the dark. Frozen solutions of the various alkylcobaloximes were evacuated, a known excess of HCl or DCl was introduced and the reaction mixtures were allowed to warm to room temperature. In all cases, mixtures of pyridinium chloride (identified by its IR and ^1H NMR spectra) and protonated alkylcobaloximes [15] precipitated. On stirring in the dark over several hours (several days for the methyl compound), the orange mixtures disappeared, to be replaced in most cases by a green precipitate of $Co(DH)(DH_2)Cl_2$. The sole exception was the reaction of the benzyl compound, which formed a blue precipitate. The latter was identified (IR, UV–vis spectra) as $(pyH)_2$-

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TABLE I. Organic Products from Reactions of Alkylcobaloximes $RCo(DH)_2py$ with Anhydrous HCl (DCl).

R	Products from HCl Cleavage	Products from DCl Cleavage
Methyl	CH_4, trace of CH_3Cl	CH_3D
Ethyl	C_2H_6, trace of C_2H_4	C_2H_5D
Isopropyl	C_3H_8, C_3H_6 (3:2)	C_3H_7D
Neopentyl	Me_4C	Me_3CCH_2D
Cyclohexyl	c-C_6H_{12}, trace of c-C_6H_{10}	c-$C_6H_{11}D$, c-$C_6H_{10}D_2$ (5:1)
cis- and *trans*-4-methylcyclohexyl	MeC_6H_{11}, trace of MeC_6H_9	See text
Benzyl	$PhCH_2CH_2Ph$, $PhCH_2Cl$ (4:1)	–

$[CoCl_4]$; it readily converted to the green $Co(DH)(DH_2)Cl_2$ on exposure of the reaction mixture to air.

In several cases, the initial uptake of HCl was measured manometrically. The organic products of the reactions were analyzed by G.C. and G.C.–M.S. techniques, as well as by NMR spectroscopy. The results are shown in Table I. The DCl cleavage reactions were usually carried out on the exchanged compounds, *Ib*; the organic products are shown in Table I.

IR spectra were run on Perkin Elmer 180 and Beckman 4240 spectrometers, NMR spectra on Bruker HX 60 and CXP 200 spectrometers, UV–visible spectra on a Perkin-Elmer 552 spectrophotometer. Gas chromatography experiments were carried out using a Hewlett Packard 5880 Gas Chromatograph with packed and capillary columns, G.C.–M.S. experiments using a Finnigan 100 quadrupole mass spectrometer with accessories.

Results and Discussion

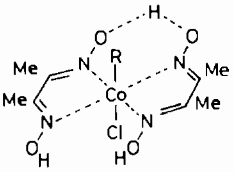
The initial reactions on exposure of the alkyl compounds $RCo(DH)_2py$ to excess (~10X) anhydrous hydrogen chloride in CH_2Cl_2 are as described in equations (2)–(4), *i.e.*

$$RCo(DH)_2py + HCl \rightarrow RCo(DH)_2 + pyH^+Cl^- \downarrow \qquad (2)$$

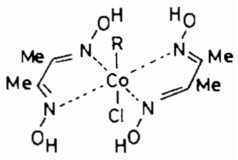
$$\underset{II}{RCo(DH)_2 + HCl \xrightleftharpoons{K_1} RCo(DH)(DH_2)Cl\downarrow} \qquad (3)$$

$$RCo(DH)(DH_2)Cl + HCl \xrightleftharpoons{K_2} \underset{III}{[RCo(DH_2)_2Cl]^+Cl^-\downarrow} \qquad (4)$$

The ^1H NMR spectra ($CDCl_3$) of the precipitates so formed showed that the DH methyl resonance of *I* (R = Me) at δ 2.12 disappeared and was replaced by new resonances at δ 2.20 and δ 2.30. These are probably attributable to the new species *II* and *III*, in which one and two oxime oxygens, respectively, have been protonated [15, 16].



II



III

Similar results were obtained for the benzyl system.

Confirmation of the presence of a cobalt–chlorine bond was made by running the far IR spectrum of the precipitate formed from the methyl compound. A new strong band appeared at 312 cm^{-1} (Nujol mull), attributable to the Co–Cl stretching frequency [18].

While K_1 and especially K_2 are known to be small in aqueous solution [17, 19], it seems reasonable that they be much larger in poorly solvating chlorinated hydrocarbons. Manometric measurements of gas uptake for several of the alkyl compounds showed that between three and four mol of HCl were absorbed per mol of alkylcobaloxime, but the data probably have little significance. The chloride ion generated in (2) and (3) would be expected to react further with HCl to form the HCl_2^- ion [20], and the free hydroxyl groups of *II* and *III* might well undergo hydrogen bonding with dissolved HCl. The chemistry is clearly very complex, and it seemed futile to attempt to study it in further detail.

On standing for several hours, the protonated alkylcobaloximes reacted further in most cases to form $Co(DH)(DH_2)Cl_2$ (*IV*) [13] and hydrocarbons, RH, the net reaction being

$$\underset{Ia}{\mathrm{RCo(DH)_2py}} + \mathrm{3HCl} \rightarrow$$

$$\underset{IV}{\mathrm{Co(DH)(DH_2)Cl_2}} + \mathrm{pyH^+Cl^-} + \mathrm{RH} \qquad (5)$$

Details of the product distributions from these reactions, as well as of the reactions of *Ib* with DCl, are shown in Table I. In several cases, the DCl reactions were carried out with the deuterium-exchanged alkylcobaloximes because H–D exchange gave significant amounts of HCl and, hence, misleading results. As can be seen from the Table, the major organic products in all cases except the benzyl system were the saturated hydrocarbons, RH (formed in ~80% yield when R = Et, ~40% when R = MeC_6H_{10}). When DCl was used, monodeuterated alkanes were found except for the two 4-methylcyclohexyl compounds, which were anomalous (see below). Olefins were minor products except for the isopropyl system, and alkyl chlorides were observed only for the methyl and benzyl systems. The latter differed from all the others in that bibenzyl, the product of alkyl coupling, was formed rather than the expected toluene.

As mentioned in the Introduction, the hydrocarbon products could be formed via a process involving homolytic cleavage of the cobalt–carbon bonds (equation (6)),

$$\mathrm{RCo(DH)_2py} \xrightarrow{\mathrm{HCl}} \mathrm{R\cdot} + \text{‘}\mathrm{Co(DH)_2py}\text{’} \qquad (6)$$

as well as via electrophilic attack. As shown previously [4], however, radical formation should result (a) in the formation of significant amounts of coupling products, (b) in the formation of significant amounts of olefins in those cases where R contains a β-hydrogen atom, and (c) in the lack of formation of deuterated products; because of the relative bond strengths, alkyl radicals cannot abstract hydrogen atoms from hydroxyl groups or from hydrogen chloride [21]. The general product distribution observed here therefore seems most consistent with intra or intermolecular electrophilic attack by hydrogen ion on the cobalt–carbon bond of the species *II* or *III*.

The cobalt-containing product, $Co(DH)(DH_2)Cl_2$, which was generally obtained in yields of 80% or better, was also the product expected on the basis of equation (1). The material obtained was identified by comparison with a sample prepared by published procedures [13]; we note a previously unreported cobalt–chlorine stretching frequency of 275 cm^{-1}.

These results stand in stark contrast with the results from other studies of electrophilic cleavage reactions of alkylcobaloximes. Several other groups have found that protonation in aqueous solution generally *deactivates* alkylcobaloximes towards electrophilic cleavage by halogens and mercury(II), and indeed, the methylcobaloxime is stable for months, sec-alkylcobaloximes for several days, in concentrated sulphuric acid [5, 15, 17, 19, 22–24]. The differences in behaviour in aqueous and organic media are undoubtedly to be attributed to the extent of solvation of the acid; solvation by water deactivates the proton by delocalizing its positive charge. Protic acid cleavage of carbon–mercury bonds in organic media is also generally retarded by added water, apparently for the same reason [25].

Attempts to determine the stereochemistry at carbon of the DCl cleavage reactions were carried out using the *cis*- and *trans*-4-methylcyclohexyl cobaloximes (*Ia*, R = $C_6H_{10}Me$). This is an approach which we have used previously [3], and is based on differences in the C–D stretching frequencies in the IR spectra of *cis*- and *trans*-4-methylcyclohexane-d_1. In both cases, however, we observed the same complex multiplet, containing at least four bands in the C–D stretching region. Analysis by G.C.–M.S. of the methylcyclohexanes so obtained showed that they were mixtures containing d_1–d_6 products (Ratios $d_0{:}d_1{:}d_2{:}d_3{:}d{:}_4d{:}_5d{:}_6 \approx 25{:}100{:}44{:}17{:}6{:}3{:}1$). The reasons for the label scrambling are not known, but a reversible β-elimination to form a hydride–olefin complex, which could exchange its hydride ligand with free DCl, seems most likely. The olefins postulated for the methylcyclohexyl and observed for the other systems (Table I) could arise from β-elimination processes, a type of reaction for which there are precedents, albeit not yet understood, in the literature [26]. However, it is not at all clear why similar scrambling does not take place with the cyclohexyl or isopropyl compounds, or why the latter produces an unusually large proportion of olefin.

The benzylcobaloxime system was quite different from the others, yielding bibenzyl and benzyl chloride, but no toluene. In addition, a blue cobalt(II) complex was obtained and identified by comparison with the UV–visible spectrum of $K_2[CoCl_4]$-(DMSO) as containing the $[CoCl_4]^{2-}$ ion. The counter ion appeared (IR) to be the pyridinium ion.

Clearly in this case homolysis and a second process became more competitive than electrophilic cleavage, results which seem consistent with the briefly reported chemistry of the same system in aqueous sulphuric acid [17]. In up to about 15% sulphuric acid solutions, monoprotonated benzylcobaloxime decomposes to predominantly products of nucleophilic attack on the α-carbon atom by water or DH_2, while in more acidic solutions the deprotonated species appears to undergo homolysis to give bibenzyl. The chemistry investigated here seems quite analogous, given that benzyl chloride would be the product expected of nucleophilic attack on the benzylic carbon by chloride ion.

Since $PhCH_2Co(DH)_2py$ is stable thermally at room temperature and is inert to attack by chloride ion, the above interpretation, if correct, requires that protonation to form compounds of type *II* or *III* both weaken the cobalt–carbon bond and activate it to nucleophilic attack. The former point is difficult to rationalize; the only crystal structure extent of a protonated alkylcobaloxime, that of $EtCo(DH)(DH_2)Cl$ [27], suggests little or no Co–C bond lengthening on comparison with data for similar unprotonated species [9]. However, cobalt–benzylic bonds do appear to be generally very weak, of the order of 20–30 kcal mol^{-1} [26], and weakening of only a few kcal mol^{-1} may be enough to induce homolysis. The cobalt–carbon bonds of the other compounds studied here may be significantly stronger than the cobalt–benzyl bond [28], and thus homolysis is not a favoured process in these cases.

The suggestion of nucleophilic attack by chloride ion on the α-carbon atom of the protonated species seems quite reasonable, as oxidized cobalt(IV) complexes of the type $[RCo(DH)_2py]^+$ are very susceptible to this mode of reaction [1]. Indeed, even neutral alkylcobaloximes apparently undergo similar reactions with the very powerful nucleophiles HS^-, MeS^-, PhS^-, $n\text{-}BuS^-$, CN^- and $PhMeN^-$ [5]. The small amounts of methyl chloride produced in the methyl system may arise in the same way (a 3:1 mixture of methane and methyl chloride is similarly formed in concentrated hydrochloric acid [5]), and it is interesting to note that it is only the methyl and benzyl cobaloximes, containing alkyl groups which normally most readily undergo nucleophilic attack, which in fact do so. The primary and secondary alkylcobaloximes do not. Similar contrasting behaviour has been found with the species $[\eta^5\text{-}C_5H_5\text{-}Fe(CO)_2R]^+$ (R = Me, $PhCH_2$, Et, n-Bu, $PhCH_2CH_2$, $Me_3CCH_2CH_2$) [29].

While this work was in progress, there appeared a very relevant communication reporting the cleavage of a series of alkylcobaloximes of type *I* by trifluoroacetic acid in chloroform [8]. The rapid formation of pyridinium trifluoroacetate and a monoprotonated alkylcobaloxime was noted, but subsequent formation of alkane, RH, took *several days* rather than hours and produced a red, high spin octahedral cobalt(II) complex, *cis*-$Co(O_2CCF_3)_2(DH_2)_2$, rather than a cobalt(III) product.

We have only briefly investigated the trifluoroacetic acid cleavage reactions, mainly by following changes in the ^1H NMR spectra in $CDCl_3$ solutions (10X excess of anhydrous CF_3CO_2H). As expected, the protonated benzylcobaloxime decomposed over several hours to produce an orange solution containing bibenzyl, a second benzyl compound which was identified as $PhCH_2O_2CCF_3$ (NMR), and a small amount (~30% yield) of a new cobalt(III) species, with a strongly deshielded methyl resonance (δ 2.71), which is probably $CF_2CO_2Co(DH)(DH_2)O_2CCF_3$ (*cf.* $Co(DH)(DH_2)Cl_2$, δ 2.34 [30]).

Interestingly, the total intensity of the DH methyl resonances decreased by about 70% during the course of the reaction (as shown by integrating the spectra relative to the pyridinium resonances). Comparison of the chemical shift of the TMS in the sample with that of TMS in pure $CDCl_3$ showed the presence of a significant susceptibility shift [31], and assuming that the paramagnetic cobalt in the solution is all present in a species of average molecular weight equal to that of *cis*-$Co(O_2CCF_3)_2(DH_2)_2$ [8], an average magnetic moment of 3.3 B.M. for the cobalt(II) was calculated. This is close to the spin only value for a high spin cobalt(II) species (3.87 B.M.) and much higher than the magnetic moments observed for low spin $Co(DH)_2L$ species [32], suggesting that we have indeed reproduced the essential aspects of the cleavage reactions reported in reference 8.

Similar experiments with $EtCo(DH)_2py$ showed that the protonated species $EtCo(DH)(DH_2)Cl$ was essentially unreacted after twenty-four hours, in contrast to the few hours required for total cleavage by hydrogen chloride, but consistent with the previous report [8]. The reasons for the differences in reactivity of the two acids are not known, but similar results have been found for alkyl–mercury compounds [25]. Whatever the reasons for the differences, the formation of cobalt(II) suggests that trifluoroacetic acid preferentially induces homolysis of the metal–carbon bond, as in equation (6).

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