PROTONATION OF ORGANOCYANOCOBALTATE(III) COMPLEXES: A NEW SYNTHESIS OF NITRILES

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The reactions of a number of organocyanocobaltate(III) complexes with acid have been studied. The complexes may be grouped into two classes on the basis of such reactions: (1) those undergoing cleavage of the organic grouping (R) to yield RH, and (2) those undergoing rearrangement to yield new complexes which release RCN on further treatment with base.

CLEAVAGE

Preparations of $K_3[Co(CN)_5(CH_2CH{=}CHR)]$ (I; R = H or CH_3) have been described[1]. Propene and 1-butene, respectively, are formed upon acidification of these complexes. Measurement of the quantity of hydrocarbon released provides a measure of the purity of the complex and indicates the stoichiometry of the preparative reaction employed. Thus, acidification of the reaction mixture obtained by adding excess allyl iodide to an aqueous solution of $[Co(CN)_5]^{3-}$ results in the formation of one molar equivalent of propene for each two equivalents of $[Co(CN)_5]^{3-}$ employed, the following reaction being indicated[2]:

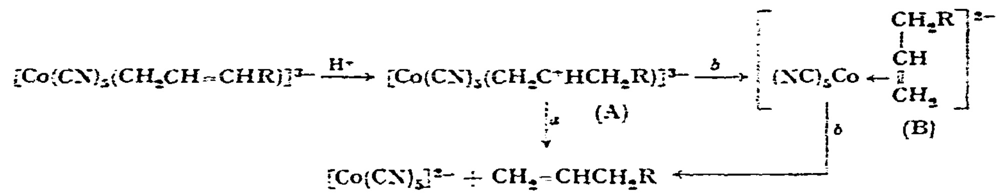
$$2[Co(CN)_5]^{3-} + CH_2{=}CHCH_2I \longrightarrow [Co(CN)_5(CH_2CH{=}CH_2)]^{3-} + [Co(CN)_5I]^{3-} \qquad (1)$$

A 94% yield of mixed allyl and halo-complexes was isolated from the reaction of $[Co(CN)_5]^{3-}$ with allyl iodide. Treatment of this solid with aqueous hydrochloric acid gave 81% of the propene expected for a 1:1 mixture of allyl and iodo-complexes (eqn. 1), partial aquation of the latter being taken into account.

Acidification of the butenyl complex isolated from the reaction of $[Co(CN)_5H]^{3-}$ with butadiene gave 69% of the 1-butene expected for a complex formed according to equation (2):

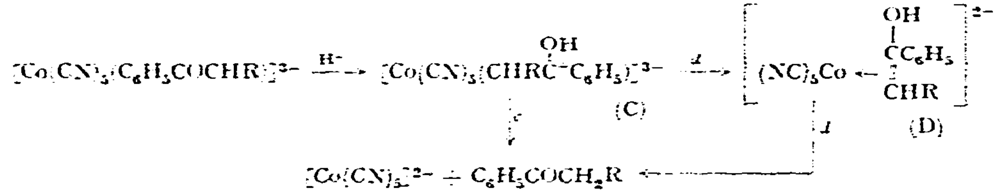
$$[Co(CN)_5H]^{3-} + CH_2{=}CHCH{=}CH_2 \longrightarrow [Co(CN)_5(CH_2CH{=}CHCH_3)]^{3-} \qquad (2)$$

The susceptibility of allylic groups attached to metal atoms to cleavage by electrophilic reagents has been discussed by Kuivila and Verdone[3]. The above protonation reactions are assumed to occur by initial formation of a carbonium ion (A) which may either eliminate olefin directly (pathway *a*) or undergo rearrangement to a π-olefin complex (B) followed by ligand displacement to yield the olefin (pathway *b*):



Postulation of the formation of π-olefin complexes stems from the isolation of such types from allylic iron[4], molybdenum[5] and tungsten[6] complexes protonated in anhydrous media. The π-olefin complexes so formed were unstable in aqueous solution, eliminating the olefin by ligand displacement. In similar manner, the π-olefin cyanocobaltate (B), a possible intermediate in the protonation of (I), would be expected to eliminate olefin under the reaction conditions employed. The exclusive formation of 1-butene[4,7] on acidification of (I) ($R = CH_3$) provides evidence for the 2-butenyl structure shown for the complex, assuming proton attack at the γ-carbon of the allylic group[4].

Preparations of $K_{x-2}[Co(CN)_x(C_6H_5COCHR)]$ (II; $R = H$ or CH_3) have been described[1]. These complexes form acetophenone and propiophenone, respectively, upon acidification. The protonations are assumed to occur in a manner similar to that shown for the allylic complexes:



Comparison may be made to the protonation of oxoalkyl iron complexes in anhydrous media, from which acidic products, formulated as π-enol complexes, were isolated[8]. These protonation products decomposed in water to reform the original oxoalkyl iron complexes. Thus, the π-enol cyanocobaltate (D), if indeed an intermediate in the protonation of (II), is more susceptible to ligand displacement than the π-enol iron complexes. Alternatively, carbonium ion (C) may eliminate ketone directly.

REARRANGEMENT

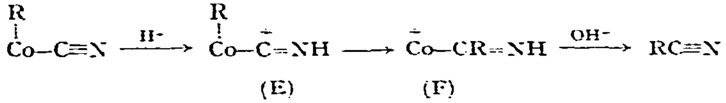
Preparations of $K_3[Co(CN)_5R]$ (III; R = n-alkyl, benzyl or phenyl) have been described[1]. It was found that these complexes do not form RH on acidification, but rather are converted to new complexes which release RCN on further treatment with alkali. For example, the benzyl complex did not produce toluene or phenylacetonitrile either on heating with alkali or on treatment with acid. However, phenylacetonitrile was formed when the acidified complex was further treated with alkali at room temperature.

To demonstrate that the nitrile was not formed during the preparation of (III) ($R = C_6H_5CH_2$) and then incorporated as such in the benzyl complex as a ligand, benzyl complex was prepared from benzyl bromide and $[Co(CN)_5]^{3-}$ in the presence of an equimolar quantity of *p*-tolylacetonitrile. The complex so obtained released only phenylacetonitrile on treatment with acid followed by base. Since it has been determined that the organic grouping (R) is directly attached to the cobalt atom in such complexes (III)[1,9], it is inferred that a rearrangement of R takes place on acidification to yield a precursor of RCN.

The product of the reaction of benzyl bromide with $[Co(CN)_5]^{3-}$ is a mixture of benzyl and halo-complexes[1]. The complexes resulting from acidification of this mixture could be separated readily into two fractions. The component more soluble in alcohol showed a single broad absorption at 2177 cm^{-1} and formed phenylacetonitrile on treatment with alkali. The less soluble component displayed an absorption at 2124 cm^{-1}, did not form nitrile on treatment with alkali and presumably was the halo-complex.

Similarly, propyl complex (III; $R = n\text{-}C_3H_7$) yielded butyronitrile, and phenyl complex (III; $R = C_6H_5$) yielded benzonitrile. It is noteworthy that the cyanocobaltate complex formed upon release of the nitriles was susceptible to oxidation and capable of catalyzing the hydrogenation of organic substrates such as α-methylstyrene. Presumably this complex is in a reduced state, since the original complexes (III) as well as other cyanocobaltate complexes of trivalent cobalt[10] do not act in this manner.

From these observations, the following reaction scheme may be outlined:



$$\overset{\displaystyle R}{\overset{|}{\text{Co}}}\text{—C}\equiv\text{N} \xrightarrow{\text{H}^+} \underset{\text{(E)}}{\overset{\displaystyle R}{\overset{|}{\text{Co}}}\text{—}\overset{+}{\text{C}}\text{=NH}} \longrightarrow \underset{\text{(F)}}{\overset{-}{\text{Co}}\text{—CR=NH}} \xrightarrow{\text{OH}^-} \text{RC}\equiv\text{N}$$

A reasonable first step is protonation at the nitrogen atom of a cyanide ligand to form a carbonium ion (E). This species could then undergo a 1,2-shift of the R group to the electron-deficient carbon atom, forming an iminocobalt complex (F). Further treatment of this complex, or perhaps a rearrangement product of (F), with alkali presumably would yield the nitrile. The cyanide stretching frequency shown by the acidified complexes is ~ 85 cm^{-1} higher than that of the non-protonated complexes[1]. Similar increases of carbonyl stretching frequencies on protonation of oxoalkyl[8] and cyanoalkyl[11] iron complexes have been described as consistent with a higher oxidation state of the metal in the protonated species. The acidified complexes also show peaks which may be due to NH stretching. Although further study of the properties of these complexes is required to establish their structures, the above reaction scheme appears to have some merit. The conversion of organocyanocobaltates to nitriles appears to be related formally to the carbonyl insertion reaction reported for methyl, benzyl and phenyl manganese carbonyls[12] and alkyl cobalt carbonyls[13].

EXPERIMENTAL

Protonation of $K_3[Co(CN)_5(CH_2CH{=}CHR)]$ ($R = H$ or CH_3)

An aqueous solution of $K_3[Co(CN)_5]$ (200 ml, 0.15 *M* cobalt, 0.35 *M* KOH, CN/Co 5.1) was prepared in an inert atmosphere as previously described[1]. Allyl iodide (0.06 mole) was injected into the stirring solution cooled by an ice-bath. After three hours, 20 ml of the reaction mixture was added to 10 ml 10% aq. HCl, whereupon 37 ml of propene was evolved (0.49 mole C_3H_6/mole cobalt). From another such reaction, 9.9 g of solid complexes was isolated. Addition of 4.0 g of the solid to 10% aq. HCl resulted in the release of 115 ml propene. Analysis of the solid for iodine (5.2%) indicated that considerable hydrolysis of $K_3[Co(CN)_5I]$ had taken place. Assuming the solid to consist of one part $K_3[Co(CN)_5(C_3H_5)]$ and one part of a mixture of $K_3[Co(CN)_5I]$ and $K_3[Co(CN)_5OH]$ (average mol. wt., 351/cobalt), the yield of propene is 81%. Complexes isolated from reactions employing allyl bromide and allyl chloride evolved 25 and 26 ml propene per gram of complex, respectively, upon treatment with acid. 2-Butenyl bromide formed a complex which evolved 16 ml 1-butene per gram. The butenyl complex isolated from the reaction of $K_3[Co(CN)_5H]$ with butadiene[1] evolved 44 ml 1-butene per gram.

Protonation of $K_3[Co(CN)_5(C_6H_5CH_2)]$

A solution (5.0 g in 20 ml H_2O) of complexes isolated from the reaction of benzyl bromide with $K_3[Co(CN)_5]$[1] was acidified (10 drops concd. HCl). The solution was then made basic and extracted with ether. The extract was dried, filtered and concentrated to yield 0.3 g phenylacetonitrile and a small quantity of phenylacetamide (m.p. 155–7°; IR spectrum). Treatment of the benzyl complex either with alkali or acid only, did not yield the nitrile. Decomposition of benzyl complex, prepared in the presence of *p*-tolylacetonitrile (equimolar to the benzyl bromide employed), by similar acid–base treatment yielded only phenylacetonitrile.

A solution (15.0 g in 100 ml H_2O) of the same complexes employed in the first experiment was acidified and added to 700 ml acetone. The white precipitate (6.2 g, Frac. 1, $C\equiv N$ stretch at 2120 cm^{-1}) was removed by filtration. The filtrate was concentrated *in vacuo*, and the gummy residue was extracted with hot ethanol. A pale yellow solid (4.3 g, Frac. 2) was removed by filtration, and the extract was concentrated to a green, viscous oil (8.5 g, Frac. 3). Ether added to a solution of the oil in ethanol precipitated a pale green solid which was dried in a high vacuum (NH stretch at 3373 cm^{-1}, $C\equiv N$ stretch at 2167 cm^{-1}). Aqueous solutions of each fraction were treated with base and extracted with ether to obtain the following quantities of phenylacetonitrile as determined by VPC: Frac. 1, 0.00 g; Frac. 2, 0.09 g; Frac. 3, 0.77 g. The latter fractions became green when base was added and rapidly turned brown at the solution surface in a manner suggesting the oxidation of $K_3[Co(CN)_5]$.

Activity toward hydrogen. A solution of benzyl complex (5.0 g in 20 ml H_2O) did not absorb hydrogen when stirred in a hydrogen atmosphere. Neither addition of α-methylstyrene (1 ml) nor subsequent addition of 10% HCl (20 ml) resulted in hydrogen absorption. Addition of alkali (8.0 g KOH in 36 ml H_2O) then turned the solution light green and 19 ml H_2 was absorbed in 7 min. Further addition of KCN (2.6 g in 7 ml H_2O) resulted in the absorption of 96 ml H_2 in 3.7 hours. Extraction of the reaction mixture with ether yielded phenylacetonitrile, α-methylstyrene and cumene, the latter two in ~ 1:1 ratio.

Protonation of $K_3[Co(CN)_5(n\text{-}C_3H_7)]$

A solution (11.2 g in 50 ml H_2O) of complexes isolated from the reaction of *n*-propyl iodide with $K_3[Co(CN)_5]$[1] was acidified and added to 350 ml ethanol. The white precipitate ($C\equiv N$ stretch at 2124 cm^{-1}) was removed by filtration and the filtrate concentrated *in vacuo*. Ether added to a solution of the residue in ethanol caused the separation of a brown oil. The oil was washed with ether and dried in a high vacuum to a brown powder (NH stretch at 3373 cm^{-1}, $C\equiv N$ stretch at 2172 cm^{-1}). Treatment of the solid with alkali, followed by ether extraction yielded butyronitrile (VPC).

Activity toward hydrogen. A solution of *n*-propyl complex (5.0 g in 20 ml H_2O) stirred in a hydrogen atmosphere did not absorb hydrogen either upon addition of α-methylstyrene (1 ml) or acidification (25 ml 10% HCl). Addition of alkali (8.0 g KOH in 36 ml H_2O) then turned the solution light green and 39 ml H_2 was absorbed in 20 min. Further addition of KCN (2.6 g in 10 ml H_2O) resulted in the absorption of 173 ml H_2 in 5.0 hours. Extraction of the reaction mixture with ether yielded butyronitrile, α-methylstyrene and cumene, the latter two in ~ 1:3 ratio.

Protonation of $K_3[Co(CN)_5(C_6H_5)]$

A solution of complexes isolated from the reaction of benzenediazonium chloride with $K_3[Co(CN)_5]$[1] yielded benzonitrile (VPC and IR spectrum) when similarly treated with acid followed by base.

ACKNOWLEDGEMENT

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SUMMARY

The protonation reactions of certain organocyanocobaltate(III) complexes have been studied. Complexes containing organic groups (R), where R = —C—C=C or —C—C=O, are cleaved to yield RH. Those containing organic groups (R′), where R′ = alkyl, benzyl or phenyl groups, undergo rearrangement to yield new complexes which release R′CN on further treatment with base. Mechanisms for these reactions are proposed and discussed.

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