

DE-ALKYLATION OF QUATERNARY AMMONIUM IONS WITH Co(I) NUCLEOPHILES

G.Costa, A.Puxeddu and E.Reisenhofer

Institute of Chemistry, University of Trieste, Trieste, Italy

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Previous work in this laboratory (1,2) has demonstrated that the transfer of a σ -bonded axial organic group can take place between two cobalt(III) atoms which differ with respect to the nature of the equatorial tetradentate ligand within a family of cobalt chelates.

The methyl group is transferred along the series of chelates from the less electrophilic to the more electrophilic cobalt atom as shown by the parallel trend of electron affinities measured by the polarographic half-wave potentials for the reversible process Co(II)-Co(I) (3).

These reactions probably occur with an S_{E2} mechanism like the previously studied de-alkylations of Co(III) corrinoids (4,5) and alkylcobaloximes (6,7) with electrophiles such as Hg^{++} , Ag^+ , Tl^{+++} . On the other hand Co(I) chelates can behave as nucleophiles with decreasing alkyl group acceptor power along the series: bae > 7,7'-Me₂salen > salen > saloph > {(do)(doh)pn} (8,9)^{*}.

In the course of a comprehensive investigation of the nucleophilic reactivity of electrochemically generated Co(I) species with organic group donors such as organic halides, we studied the behaviour of electrochemically generated Co(I) chelates towards S-alkylsulphonium and N-alkylnitrogen compounds.

When the reduction of $[Co(II)salen]^0$ ($10^{-3}M$ in dimethylformamide-LiClO₄ 0.2 M, at 0°C) is performed at controlled potential corresponding to the reduction to Co(I) species (-1.2 V vs. S.C.E.) in the presence of 20 to 30-fold excess of $[R'NR_3]^+(ClO_4)^-$ ($R' = C_6H_5CH_2-$ or C_6H_5- , $R = CH_3-$), the corresponding $[R'Co(salen)DMF]^0$ and the amine NR₃ are formed with the consumption of 1F/mole.

The organometallic complex is reduced at a more negative potential and could be identified through its characteristic polarographic $E_{1/2}$ (3) at -1.25 V for

*: bae : N,N'-ethylenebis(acetylacetonimine); 7,7'-Me₂salen : N,N'-ethylenebis(7,7'-dimethylsalicylideneimine); salen : N,N'-ethylenebis(salicylideneimine); saloph : N,N'-o-phenylenebis(salicylideneimine); {(do)(doh)pn} : 1-diacetylmonoximateoimino-3-diacetylmonoximeiminopropane.

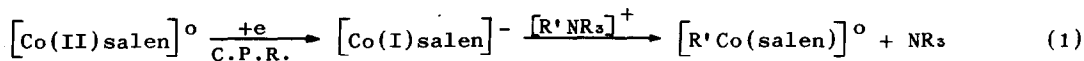
$[\text{C}_6\text{H}_5\text{CH}_2\text{Co}(\text{salen})\text{DMF}]^0$ and -1.42 V for $[\text{C}_6\text{H}_5\text{Co}(\text{salen})\text{DMF}]^0$.

The amine was displaced from the solution by gaseous nitrogen, trapped in dichloroethane containing CH_3J , crystallized and identified by its I.R. spectrum and elemental analysis.

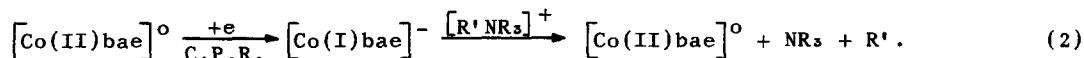
When the controlled potential reduction was performed using $[\text{Co}(\text{II})\text{bae}]^0$ in a manner corresponding to the reduction to $[\text{Co}(\text{I})\text{bae}]^-$ (-1.6 V) in the presence of $[\text{N}(\text{CH}_3)_4]^+(\text{ClO}_4)^-$ or $[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_3]^+(\text{ClO}_4)^-$, a catalytic reduction of the ammonium salt was observed. When the electrolysis was stopped the cobalt complex was still present as $[\text{Co}(\text{II})\text{bae}]^0$ as revealed by polarography. Trimethylamine was identified as above and toluene was recovered from de-alkylation of $[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_3]^+(\text{ClO}_4)^-$ and identified by g.l.c. From $[\text{N}(\text{CH}_3)_4]^+(\text{ClO}_4)^-$ methane and trimethylamine were obtained. Kinetic measurements are in progress.

The present results show that two distinct reaction paths can be observed depending on the nature of the equatorial chelating group.

In the case of salen the transfer of the organic group from nitrogen to the cobalt atom can be envisaged as a binuclear nucleophilic displacement ($\text{S}_{\text{N}2}$) by attack of $[\text{Co}(\text{I})\text{salen}]^-$ on the saturated carbon atom :



In the case of the more nucleophilic $[\text{Co}(\text{I})\text{bae}]^-$ the electron transfer leads to the formation of the $\text{Co}(\text{II})$ species, and of the $\text{R}'\text{NR}_3$ radical which undergoes homolytic fission and release of the R' radical as in the electrolysis of $[\text{R}'\text{NR}_3]^+$. The latter occurs even in the absence of cobalt chelates but at very negative potentials. The benzyl radical is known to give toluene in DMF (10).



The reactions reported here extend the scope of the Vit.B₁₂ model compounds to include also the alkyl transfer reaction from nitrogen donors to the $\text{Co}(\text{I})$ species. The remarkable feature of the methionine biosynthesis is the requirement of both the cofactor S-adenosyl-L-methionine and the N⁵-methyl tetrahydrofolate as methyl donors and the cobalamin, perhaps in the cobalt (I) oxidation state, as the acceptor. The details of this process are still unclear and one especially interesting point is thus the mechanism of the alkyl group transfer

from sulphur and nitrogen atoms to Co(I) species. The transfer of alkyl groups from sulphonium and ammonium compounds had previously been observed only for cobaloximes (11,12).

Present results show that the C-N bond in quaternary ammonium salts can be catalytically cleaved by the Co(I) species.

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