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Preliminary communication

CONCERNING THE OXIDATION MECHANISM OF ALKYLCOBALT CHELATES

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Summary

Studies in electrooxidation of alkylbis(salicylidenato)ethylenediaminecobalt(III) allowed various complicated processes of oxidative cleavage of organocobalt chelates to be elucidated in terms of a single mechanism. The electron transfer was followed by reactions of the organocobalt(IV) intermediate with available nucleophiles including the initial cobalt(III) complex.

While the oxidatives cleavage of the metal—carbon σ-bond in organocobalt chelates, RCo^{III}(chel), containing a tetradentate dianion $(chel)^{2-}$ have been studied rather thoroughly [1—7], there is much discussion concerning the mechanism of these processes which is evidently due to the wide diversity of observed products. Thus, the reactions with halogens (Cl_2, Br_2, I_2, ICl) give not only "normal" products (organic halides RX and "inorganic" chelates of trivalent cobalt, $[Co^{III}(chel)]^+$, but also chelates of the divalent metal Co^{II}(chel), olefins R_{-H} and vicinal dihalides $R_{-H}X_2$ with R = alkyl and coupled radicals R_2 with R = benzyl. Furthermore, products of solvolysis (e.g. alcohols ROH in the case of aqueous solutions) and products resulting from alkylation of a chelating ligand (viz. dimethyl glyoximate) were observed. To elucidate these results, several mechanisms for the oxidative splitting of the Co—C bond were proposed: direct electrophilic substitution at the α-carbon [1, 5—7]; radical attack at the metal ion [5] or α-carbon [7] and one-electron oxidation followed by electrophilic attack at the intermediate complex of tetravalent cobalt $[RCo^{IV}(chel)]^+$ [3—5]. Some authors suggest that the reactions proceed by at least two parallel mechanisms [5, 7]. Nevertheless, ways leading to olefins and especially to the products of alkylation of chelating ligands have so far not been elucidated.

Our studies carried out with electrochemical techniques indicate that both anodic and homogeneous chemical oxidations of the alkylcobalt chelates RCo^{III}(chel) can be interpreted in terms of a single mechanism, with rupture of

TABLE 1

ELECTROOXIDATION OF ALKYLCOBALT(III) CHELATES[a]

Complex	Potential (volts)[b]	Charge transferred (Faradays per mol of the initial complex)	Yield of products (mols per mol of the initial complex)		
			Chelate[e]	Olefin R–H	Chelating ligand alkylation product[g]
$CH_3CoSalen$	+0.78[c]	1.45[d]	$[Co^{III}Salen]^+$, 0.56		o-$CH_3OC_6H_4CHO$, 0.06
$C_2H_5CoSalen$	+0.75[c]	1.50[d]	$[Co^{III}Salen]^+$, 0.44	Ethylene[f]	o-$C_2H_5OC_6H_4CHO$, 0.44
n-$C_4H_9CoSalen$	+0.75[c]	1.54[d]	$[Co^{III}Salen]^+$, 0.49	But-1-ene, 0.48[f]	o-$C_4H_9OC_6H_4CHO$, 0.50

[a] Controlled potential oxidations were carried out at a platinum electrode with 0.1 *M* $NaBF_4$ in MeCN as supporting electrolyte at 20 °C. [b] Versus SCE. [c] Plateau potential. [d] Current has dropped more than 100 times in comparison with the initial value. [e] Voltammetry data. [f] GLC analysis. [g] After acidic hydrolysis of the anolyte, the products were identified with both TLC (on alumina) and GLC (column: 4% of Carbowax 20M on Chromosorb G); quantitative analyses were performed using the latter technique.

ligand. It should be pointed out in this connection that the RCo^{III}Salen complexes are known to feature nucleophilic reactivity localized at oxygen atoms within the chelating ligand. This type of reactivity is manifest when the alkylcobalt(III) chelates are protonated [10] or give complexes with metal ions [11].

These facts enabled us to develop Scheme 1 for the anodic process in the absence of sufficiently active "external" nucleophiles. In this case the electron transfer (1) is followed by alkylation of the chelating ligand in the initial cobalt(III) compound with the tetravalent metal complex (2)*. Subsequent steps involve elimination of olefin from the *O*-alkylated complex where the metal—carbon bond should be labilized in view of accessibility of the *cis*-position (3), and oxidations of certain chelate intermediates, (4) and (5). The proposed scheme for the anodic reaction suggests consumption of 1.5 Faradays per mol of the initial complex and formation of the trivalent cobalt chelate $[Co^{III}Salen]^+$, olefin $\bar{R}_{-H}$ and alkylated product in equal (0.5 mol) yields. The experimental data for the ethyl- and n-butyl-cobalt complexes follow this pattern reasonably well, while the methylcobalt compound deviates sharply and seems to present a special case (Table 1).

References

1 F.R. Jensen, V. Madan and D.H. Buchanan, J. Amer. Chem. Soc., 92 (1970) 1414.
2 D. Dodd and M.D. Johnson, J. Chem. Soc. Chem. Commun., (1971) 571.
3 P. Abley, E.R. Dockal and J. Halpern, J. Amer. Chem. Soc., 94 (1972) 659.
4 S.N. Anderson, D.H. Ballard, J.Z. Chrzastovski, D. Dodd and M.D. Johnson, J. Chem. Soc. Chem. Commun., (1972) 685.
5 D. Dodd and M.D. Johnson, J. Organometal. Chem., 52 (1973) 1 and refs. therein.
6 M. Tada and H. Ogava, Tetrahedron Lett., (1973) 2639.
7 R. Dreos, G. Tauzher, N. Marich and G. Costa, J. Organometal. Chem., 92 (1975) 227.
8 I.Ya. Levitin, A.L. Sigan and M.E. Vol'pin, Izv. Akad. Nauk SSSR Ser. Khim., (1974) 1205; J. Chem. Soc. Chem. Commun., (1975) 469.
9 J. Halpern, M.S. Chan, J. Hanson, T.S. Roche and J.A. Topich, J. Amer. Chem. Soc., 97 (1975) 1606.
10 G. Tauzher, R. Dreos, G. Costa and M. Green, J. Organometal. Chem., 81 (1974) 107.
11 G.R. Tauszik, G. Pellizer and G. Costa, Inorg. Nucl. Chem. Lett., 9 (1973) 717.

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*An inner sphere rearrangement of the cobalt(IV) complex could also lead to alkylation of the chelating ligand. However, this route seems unlikely, since nucleophilicity of the ligand should depend heavily on the oxidation state of the metal. Moreover, this mechanism does not explain formation of the olefin.