DALTON

Electrochemical carboxylation of arylmethyl chlorides catalysed by [Co(salen)] [H_2salen = *N,N'*-bis(salicylidene)ethane-1,2-diamine]

Abdirisak Ahmed Isse, Armando Gennaro and Elio Vianello *

Dipartimento di Chimica Fisica, via Loredan 2, 35131 Padova, Italy

The electrochemical carboxylation of some arylmethyl chlorides RCl [R = benzyl, 4-methoxybenzyl, 4-(trifluoromethyl)benzyl or diphenylmethyl] catalysed by [Co(salen)] [H_2salen = *N,N'*-bis(salicylidene)-ethane-1,2-diamine] was studied in acetonitrile. Comparable amounts of carboxylic acids and saturated hydrocarbons were obtained when R = $PhCH_2$ or 4-$MeOC_6H_4CH_2$ whereas carboxylic acids were the main products with R = 4-$F_3CC_6H_4CH_2$ or Ph_2CH. Electrogenerated $[Co^I(salen)]^-$ reacts with RCl to give an organometallic complex, $[Co^{III}(salen)R]$, with a rate constant which, for all chlorides investigated, is of the order of 10^5 dm^3 mol^{-1} s^{-1}. The one-electron-reduced complex $[Co^{II}(salen)R]^-$ is unstable and its decomposition in the presence of CO_2 is the key step of the electrocatalytic process. Different decomposition pathways are considered and their mechanistic implications discussed. In the presence of proton donors $[Co^{II}(salen)R]^-$ undergoes rapid hydrolysis to RH and [Co(salen)].

The electroreductive carboxylation of organic halides with carbon dioxide is an interesting method of synthesis of carboxylic acids. However, direct reduction of organic halides in CO_2-saturated aprotic solvents gives only moderate yields of carboxylic acids.[1] Very often, together with the carboxylic acids, considerable amounts of esters resulting from a chemical reaction between the carboxylate ions and the unreacted halides were obtained. Use of sacrificial anodes, which hinders this side reaction, was found to improve considerably the yields of carboxylic acids.[2] Electrocarboxylation of a wide variety of organic halides in CO_2-saturated dimethylformamide has been accomplished with high yields in undivided cells fitted with sacrificial aluminium or magnesium anodes.[2,3]

Catalytic systems based on transition-metal complexes have also been proposed in order to improve the yield and selectivity of electrocarboxylations. Several nickel and palladium complexes have shown good catalytic properties in electroreductive carboxylation of various aromatic and benzylic halides.[4]

Square-planar cobalt complexes have been extensively studied as potential catalysts for the activation of organic halides. It is well known that nucleophilic cobalt(I) complexes readily react with organic halides through an S_N2 mechanism to give the corresponding organometallic complexes.[5] Electrochemical reduction of these complexes has been investigated by several groups.[6] It has been shown that, upon one-electron reduction, such organocobalt complexes undergo cobalt–carbon bond cleavage whereby the original cobalt complex is regenerated. Electroreduction of various organic halides has been reported to be catalysed by [Co(salen)] [H_2salen = *N,N'*-bis(salicylidene)ethane-1,2-diamine].[6b,7] Analogously, [Co(salophen)][8] [H_2salophen = *N,N'*-bis(salicylidene)-*o*-phenylenediamine] has been used as catalyst in the electroreduction of benzyl chloride to toluene. However, preparative reduction of this complex in the presence of a 10-fold excess of $PhCH_2Cl$ carried out at the reduction potential of [Co(salophen)-(CH_2Ph)] has been reported to give 31% of C_6H_5Me with total decomposition of the catalyst after a few catalytic cycles.

Notwithstanding the extensive work devoted to cobalt(I)-mediated reduction of organic halides, cobalt(I) complexes have received little interest as catalysts for electrochemical carboxylation of organic halides. Electrocarboxylation of some benzylic and allylic chlorides has been shown to be catalysed by [Co(salen)][9] in tetrahydrofuran–hexamethylphosphoramide [thf–$P(NMe_2)_3O$] containing $LiClO_4$ as background electrolyte. We describe in this paper a detailed study of the mechanism of electrochemical carboxylation of some arylmethyl chlorides RCl [R = 4-(trifluoromethyl)benzyl **1**, diphenylmethyl **2**, benzyl **3** or 4-methoxybenzyl **4**] in acetonitrile catalysed by [CoL] (L = salen).

Experimental

Acetonitrile was distilled over CaH_2 and stored under an argon atmosphere. Before use, the solvent containing the background electrolyte was repeatedly percolated through a column of neutral alumina previously activated by heating under vacuum at 360 °C overnight. Tetra-*n*-butylammonium perchlorate (Fluka) was recrystallised twice from ethanol–water (2:1) and dried at 60 °C under vacuum. The complex [CoL] was prepared as described in the literature.[10] Commercially available reagent-grade arylmethyl chlorides were used as received. The solubility of CO_2 in acetonitrile was previously determined as 0.28 mol dm^{-3} at 25 °C and under a carbon dioxide atmosphere.[11]

Electrochemical measurements were carried out with an EG&G apparatus comprising a 173 potentiostat and a 179 digital coulometer and equipped with an Amel 568 function generator and a Nicolet 206 oscilloscope. The cell and electrodes used have been described.[6d] All experiments were carried out in MeCN with 0.1 mol dm^{-3} $[NBu^n_4]ClO_4$ at 25 °C. The electrolysis products were analysed by using either an HPLC Perkin-Elmer Series 4 liquid chromatograph equipped with a UV detector and a reversed-phase ODS2 column or a Varian 3700 gas chromatograph with a Supelco column GP 10% SP-1200, 1% H_3PO_4.

Results

Voltammetry of [CoL] in MeCN containing 0.1 mol dm^{-3} $[NBu^n_4]ClO_4$ as supporting electrolyte shows a reversible peak couple, noted as A/B in Fig. 1(*a*), which represents the redox couple $[Co^{II}L]$–$[Co^IL]^-$ with $E^\circ = -1.29$ V *vs.* saturated calomel electrode (SCE). Addition of an arylmethyl halide such as **3** strongly modifies the voltammetric pattern of the complex. Peak A is shifted to less negative potentials, its anodic partner B disappears completely while a new cathodic peak C appears at more negative potentials [Fig. 1(*b*)]. In the presence of a large excess of RCl the potential of peak A, E_p(A), is shifted by *ca.* 30 mV in the negative direction and by *ca.* 30 mV in the positive direction, for a ten-fold increase in the sweep rate and the halide concentration, respectively. This behaviour is indicative of a chemical reaction between the electrogenerated Co^I and RCl. Square-planar cobalt(I) complexes are strong nucleophiles and their reactivity towards organic halides to give organocobalt complexes is well documented.[5] Therefore, in the presence of RCl, the sequence of reactions (1) and (2) is expected to occur at peak A.

$$[Co^{II}L] + e^- \rightleftharpoons [Co^IL]^- \qquad (1)$$

$$[Co^IL]^- + RCl \xrightarrow{k_2} [Co^{III}L(R)] + Cl^- \qquad (2)$$

The rate constant of reaction (2) can be calculated from the dependence of $E_p(A)$ upon the scan rate v and concentration of RCl. In the presence of an excess of RCl sufficient for reaction (2) to be pseudo-first order the peak potential is given, under pure kinetic conditions,[12] by equation (3) where $k_2' = k_2[RCl]$, E° is the standard potential of the redox couple $[Co^{II}L]$–$[Co^IL]^-$ and $n = 1$ for the case under discussion. The pseudo-first-order rate constant k_2' was calculated at different RCl concentrations and at several sweep rates for each [RCl]. The average of the values of the rate constants k_2 obtained at different RCl concentrations are reported in Table 1. They do not differ very much and are of the same order as that for the reaction between $[Co^I(salophen)]^-$ and Bu^nI.[6d]

$$E_p = E^\circ - \frac{0.78RT}{nF} + \frac{RT}{2nF}\ln\frac{RTk_2'}{nF\nu} \qquad (3)$$

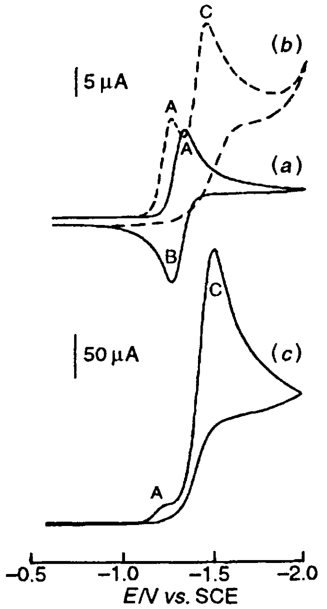

Fig. 1 Cyclic voltammograms at a mercury electrode of [Co(salen)] in MeCN + 0.1 mol dm^{-3} $[NBu^n{}_4]ClO_4$ at $v = 0.2$ V s^{-1}: (*a*) 0.97 mmol dm^{-3} [Co(salen)], (*b*) as (*a*) + 10.4 mmol dm^{-3} $PhCH_2Cl$, (*c*) as (*b*) in the presence of 21.4 mmol dm^{-3} PhOH

Reduction of the organometallic product of reaction (2), equation (4), gives rise to peak C [see Fig. 1(*b*)]. Peak potentials are listed in Table 1. Peak C shows no anodic partner up to high scan rates, indicating that the species $[Co^{II}L(R)]^-$ is unstable, even on the time-scale of rapid cyclic voltammetry. As previously observed for various organocobalt complexes,[6,14] the one-electron reduction product is expected to undergo rapid Co–C bond cleavage. The process can be homolytic [equation (5)] or heterolytic [equation (6)] depending mainly on the electron-donor properties of the R moiety.[14] Organocobalt complexes bearing good electron-withdrawing groups give carbanions upon dissociation whereas the radical mode is preferred with electron-donating groups. As to the (arylmethyl)cobalt complexes studied in this work, no clear evidence has been reported helping to discriminate between the above alternatives. However an indication as to the difference between the driving forces of the two modes of Co–C bond breaking can be gained by an appropriate choice of thermodynamic cycles, involving the following reactions (7) and (8) together with (1) and (4)–(6). It can easily be verified that $\Delta G^\circ_5 = \Delta G^\circ_7 + F(E^\circ_4 - E^\circ_1)$ and $\Delta G^\circ_6 = \Delta G^\circ_7 + F(E^\circ_4 - E^\circ_8)$. Although the separate values of ΔG°_5 and ΔG°_6 cannot be calculated since neither ΔG°_7 nor E°_4 is available, their difference $\Delta G^\circ_5 - \Delta G^\circ_6 = F(E^\circ_8 - E^\circ_1)$ is provided by the E° difference of the redox couples $[Co^{II}L]$–$[Co^IL]^-$ and $R^\bullet$–R^-. The reduction potentials of several arylmethyl radicals have recently been measured by means of photoelectrochemical techniques.[13] By using literature values of the redox potentials of the $R^\bullet$–R^- redox couples and the value of E°_1 we measured, the difference in ΔG° values of reactions (5) and (6) was calculated. The results are reported in Table 1. The standard reduction potential of 4-(trifluoromethyl)benzyl radical, which had not been determined experimentally, has been estimated from the Hammett correlation between standard reduction potentials of ring-substituted benzyl radicals[13a] and σ^- of the substituents. Although the $\Delta G^\circ_5 - \Delta G^\circ_6$ values are not high, on the basis of the above thermodynamic considerations decomposition of benzyl- and 4-methoxybenzyl-cobalt complexes is expected to follow a radical pathway, whereas the opposite mode of Co–C bond breaking appears to be more favourable for diphenylmethyl- and 4-(trifluoromethyl)benzyl-cobalt complexes.

$$[Co^{III}L(R)] + e^- \rightleftharpoons [Co^{II}L(R)]^- \qquad (4)$$

$$[Co^{II}L(R)]^- \longrightarrow R^\bullet + [Co^IL]^- \qquad (5)$$

$$[Co^{II}L(R)]^- \longrightarrow R^- + [Co^{II}L] \qquad (6)$$

$$[Co^{III}L(R)] \longrightarrow R^\bullet + [Co^{II}L] \qquad (7)$$

$$R^\bullet + e^- \rightleftharpoons R^- \qquad (8)$$

It should be noted, on the other hand, that whatever the Co–C bond-breaking mode, the species $[Co^IL]^-$ is expected to

Table 1 Rate constants for formation of $[Co^{III}L(R)]$ and difference in free-energy changes between the two Co–C bond-breaking modes of $[Co^{II}(salen)R]^-$ [a]

R	E_p[b]$[CoL(R)]$/V *vs.* SCE	$10^{-5}k_2/dm^3\ mol^{-1}\ s^{-1}$	$E^\circ(R^\bullet-R^-)$/V *vs.* SCE	$\Delta G^\circ_5 - \Delta G^\circ_6$/kJ mol^{-1}
$4-F_3CC_6H_4CH_2$	−1.38	1.0 ± 0.3	−1.09	19.3
Ph_2CH	−1.34	3.2 ± 0.3	−1.14[c]	14.5
$PhCH_2$	−1.45	1.1 ± 0.1	−1.43[c]	−13.5
$4-MeOC_6H_4CH_2$	−1.51	1.2 ± 0.1	−1.75[d]	−44.4

[a] $E^\circ = -1.29$ V *vs.* SCE for $[Co^{II}L]$–$[Co^IL]^-$. [b] Potential of the reduction peak of $[Co^{III}L(R)]$ measured at $\nu = 0.2$ V s^{-1}. [c] Taken from ref. 13(*b*). [d] Taken from ref. 13(*a*).

be formed, either directly [equation (5)] or after reduction of [Co^{II}L] stemming from reaction (6). Since the organometallic complex should be reformed through the rapid reaction (2), this would imply a catalytic transformation of RCl, taking place at the reduction potential of [Co^{III}L(R)]. The voltammetric results show, on the contrary, that even though decomposition of [Co^{II}L(R)]$^-$ appears to be rapid, the current at peak C is quite low even in the presence of a large excess of RCl with respect to [CoL]. In the case of compound **3**, for example, cyclic voltammetry of [CoL] containing *ca.* 10 equivalents of the halide shows two irreversible reduction peaks, the one due to the organometallic complex being only slightly higher than that of the one-electron reduction of [CoL] [Fig. 1(*b*)]. Controlled-potential electrolysis carried out at the potential of [Co(L)(CH$_2$Ph)] resulted in complete deactivation of the catalyst after a few catalytic cycles. Of the benzyl chloride consumed up to that point, 32.8% was transformed into toluene and 6.5% into bibenzyl. Similar results have been previously reported using [Co(salophen)] as catalyst.[8] Such a low catalytic efficiency is attributable to some parasitic reaction involving the reduction intermediates, which destroys the catalyst.[15]

Although catalytic reduction of RCl to RH by [CoL] is very poor in dry acetonitrile, addition of proton donors considerably improves the catalytic efficiency of the system. In the presence of water, phenol or acetic acid the reduction peak C of the organometallic compound increases while that of [CoL] remains practically unaffected. Fig. 1(*c*) shows as an example the voltammetric behaviour of [CoL] in the presence of benzyl chloride and phenol. The effect of the added proton donor is to increase considerably peak C. Similar current enhancements, observed with the other halides investigated, are reported in Table 2. Controlled-potential electrolyses carried out at the potential of [CoL(R)] in the presence of water led to the formation of saturated hydrocarbons RH in high yields (see below).

Saturation of a [Co^{II}L] solution with CO$_2$ does not modify substantially the voltammeric pattern of the complex. The latter keeps, in fact, its full reversibility without any appreciable peak potential shift, showing that interaction of CO$_2$ with both the oxidised and reduced forms of the complex is negligible, at least on the voltammetric time-scale. This is in agreement with previous reports showing that the reactivity of CO$_2$ towards cobalt(I) Schiff-base complexes is greatly influenced by the nature of the associated cation.[16–18] Small alkali-metal cations, such as Li$^+$ and Na$^+$, promote the formation of Co–CO$_2$ adducts, through co-ordination of an oxygen atom of a CO$_2$ molecule which is carbon bound to the cobalt centre.[16] These alkali-metal cations favour also the reduction of CO$_2$ to CO, catalysed by cobalt(I) complexes of salen[17a] and salophen.[17b] On the contrary, low binding constants have been found with bulkier alkylammonium cations.[18]

However, when CO$_2$ is added to [Co^{II}L] solution also containing RCl, the reduction peak of the organocobalt complex is substantially enhanced. Fig. 2 shows cyclic voltammograms of [CoL] recorded in the presence of an excess of diphenylmethyl chloride either under argon or under a carbon dioxide atmosphere. The peak current ratios i_p/i°_p measured in the presence of CO$_2$ are included in the data presented in Table 2. The current enhancements are comparable with those caused by water and both are substantially higher with halides **1** and **2**.

Controlled-potential electrolysis of CO$_2$-saturated acetonitrile solutions containing about 1 mmol dm^{-3} [CoL] and RCl in large excess, carried out at the reduction potential of [CoL(R)], led to a sustained catalysis with formation of carboxylic acid RCO$_2$H and saturated hydrocarbon RH. The electrolyses were interrupted after total conversion of the halide was achieved, which required the consumption of 2.05 F per mol of RCl, while the original [CoL] was substantially unaltered. During electrolysis the solution was red-brown which turned to the typical deep green of cobalt(I) complexes as soon as RCl was consumed and [Co^{I}L]$^-$ started to accumulate. The results of preparative-scale reduction experiments are summarised in Table 3. For chlorides **3** and **4** comparable amounts of carboxylic acid and saturated hydrocarbon were obtained together with trace amounts of bibenzylic dimers. Reduction of **1** and **2** yields mainly the carboxylated products. Formation of ester by reaction of the carboxylate ion RCO$_2$$^-$ with unreacted halide was never observed. In the case of chlorides **3** and **4** the ratio RCO$_2$H : RH varies with the applied electrolysis potential. Since no particular attention was paid to position the reference electrode as near as possible to the working electrode, in order to minimise the uncompensated ohmic drop, it is possible that the real potential between the two electrodes was *ca.* 100 mV more positive than the applied potential. It is clear, however, from the results collected in Table 4 that the relative yield of the acid increases with decreasing electrolysis potential.

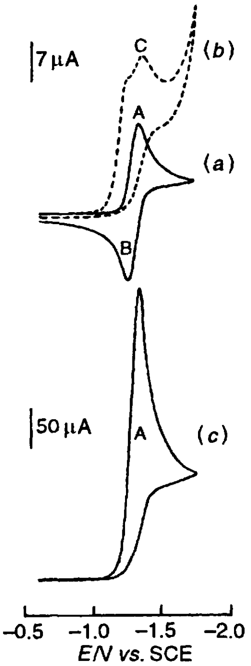

Fig. 2 Cyclic voltammograms at a mercury electrode of [Co(salen)] in MeCN + 0.1 mol dm^{-3} [NBu$^n_4$]ClO$_4$ at v = 0.2 V s^{-1}: (*a*) 1.18 mmol dm^{-3} [Co(salen)], (*b*) as (*a*) + 9.8 mmol dm^{-3} Ph$_2$CHCl and (*c*) as (*b*) in the presence of CO$_2$ (0.28 mol dm^{-3})

In order to verify whether the background electrolyte plays any role in the process, the solution in which compound **3** had been electrolysed was analysed for NBu$^n_3$. The latter was found in a quantity corresponding to *ca.* 65% of the toluene formed.

The effect of water on the electrochemical carboxylation of the halides catalysed by [CoL] was also examined. The results are reported in Table 3. In the presence of this proton donor, RH is obtained as the major reduction product. It is interesting that electrolysis of compound **3** in the presence of 1 mol dm^{-3} D$_2$O yields 80% deuteriated toluene.

Discussion

The scanty interaction between CO$_2$ and [Co^{I}L]$^-$ under our experimental conditions and the high values of the rate constants k_2 reported in Table 1 clearly indicate that the first step of the electrocatalytic carboxylation of arylmethyl chlorides is the fast reaction (2) between the electrogenerated [Co^{I}L]$^-$ and RCl. One-electron reduction of the ensuing organometallic complex yields the unstable species [Co^{II}L(R)]$^-$, the decomposition of which in the presence of CO$_2$ is the key step of the catalytic cycle. This step may consist in a direct

Table 2 Current enhancements of the reduction peak of [Co(salen)R] caused by addition of anion traps

R	[RCl]/mmol dm^{-3}	[CoL]/mmol dm^{-3}	A	[A]/mol dm^{-3}	i_p/i°_p*
4-$F_3CC_6H_4CH_2$	8.80	0.88			1.1
	9.46	0.94	Water	1.0	19.5
	8.80	0.88	CO_2	0.28	26.1
Ph_2CH	12.09	1.27			1.0
	40.78	0.96	Water	1.0	26.8
	9.56	0.94	CO_2	0.28	24.6
$PhCH_2$	9.56	0.97			1.8
	9.56	0.97	CO_2	0.28	3.9
	13.03	1.15	Water	1.0	3.8
	9.56	0.97	$MeCO_2H$	0.014	17.1
	9.56	0.96	PhOH	0.025	18.8
4-$MeOC_6H_4CH_2$	14.01	1.42			2.6
	9.59	0.98	Water	1.0	7.4
	14.01	1.42	CO_2	0.28	5.8

* i_p is the peak current for the reduction of $[Co^{III}L(R)]$ measured in the presence of RCl and A; i°_p is the peak current for the reduction of [CoL] measured before the addition of RCl.

Table 3 Electrocarboxylation of RCl catalysed by [Co(salen)] in CO_2-saturated acetonitrile; [A] = 1.0 mol dm^{-3}

					Product (%)[b]	
R	[RCl]/mmol dm^{-3}	[CoL]/mmol dm^{-3}	A	E^a/V	RCO_2H	RH
4-$F_3CC_6H_5CH_2$	8.36	0.84		−1.59	84.3	13.8
	9.46	0.94	Water	−1.59	3.3	90.5
Ph_2CH	12.09	1.27		−1.34	92.6	0
	8.84	0.95	Water	−1.34	22.7	72.3
$PhCH_2$	13.03	1.11		−1.61	43.7	49.3
	12.17	2.82	Water	−1.61	8.3	89.8
	17.35	1.15	D_2O	−1.61	9.7	62.8[c]
4-$MeOC_6H_4CH_2$	8.85	0.89		−1.86	38.0	37.6
	8.11	0.81	Water	−1.86	8.2	64.0

[a] Electrolysis potential (*vs.* SCE). [b] The yield is calculated with respect to RCl. [c] 80% Toluene is deuteriated.

Table 4 Effect of applied potential in the electrochemical carboxylation of arylmethyl chlorides catalysed by [Co(salen)] in CO_2-saturated acetonitrile

				Product (%)[b]		
R	[RCl]/mmol dm^{-3}	[CoL]/mmol dm^{-3}	E^a/V	RCO_2H	RH	RCO_2H:RH
$PhCH_2$	10.42	1.84	−1.52	34.6	53.4	0.65
	12.60	1.28	−1.56	41.4	51.2	0.81
	13.03	1.11	−1.61	43.7	49.3	0.89
	21.72	1.09	−1.68	48.2	49.6	0.97
	16.04	1.30	−1.81	46.4	42.5	1.09
4-$MeOC_6H_4CH_2$	11.06	1.13	−1.64	27.9	44.9	0.62
	8.85	0.89	−1.86	38.0	37.6	1.01

[a] Electrolysis potential (*vs.* SCE). [b] The yield is calculated with respect to RCl.

attack of CO_2 on $[Co^{II}L(R)]^-$, followed by or concerted with bond breaking to give carboxylate and $[Co^{II}L]$. On the other hand, owing to the intrinsic instability of the intermediate $[Co^{II}L(R)]^-$, it is also conceivable that Co–C bond breaking in the latter, either homolytic or heterolytic, precedes any interaction of the arylmethyl moiety with CO_2.

As observed above, most of the experimental results show significant differences between compounds **1** and **2**, on the one hand, and **3** and **4**, on the other. The latter in particular gave relatively modest current enhancements upon addition of CO_2 (see Table 2) and yielded comparable amounts of carboxylic acid and hydrocarbon upon electrolysis (see Table 3). Let us try to discuss these results in terms of the mechanism involving Co–C bond breaking prior to interaction with CO_2. The formation of the carboxylated products suggests the intermediacy of carbanions R^-, which are trapped by CO_2. Saturated hydrocarbons, on the other hand, could arise from protonation of R^- by any proton donor in the reaction medium as well as from hydrogen-atom abstraction by $R^\bullet$ from the solvent. Acetonitrile is known to act as an H-atom donor towards organic radicals.[19,20] In particular, benzyl radicals formed during electroreduction of benzyl iodide in acetonitrile have been reported to give toluene through H-atom abstraction from the solvent.[19] In other words, our results seem to be compatible with both Co–C bond-breaking modes. However, owing to the very low amount of residual water in the carefully dehydrated acetonitrile, carbanions R^- could only be protonated by the solvent or by the background electrolyte. Although acetonitrile is a relatively 'acid' solvent and tetraalkylammonium cations are known to release protons to strongly basic reduction intermediates, through Hofmann elimination,[21] R^- are expected to undergo carboxylation rather than proton transfer in the presence of a strong electrophile such as CO_2. This is in agreement with the results obtained in the reduction of benzyl iodide in CO_2-saturated acetonitrile, *i.e.* under conditions very similar to ours, showing that, by electrolysis at a potential where R^- is produced, the carboxylated product is essentially formed.[19] This would indicate that, at least in the presence of

CO_2, the relevant quantity of RH produced should derive from $R^{\bullet}$ abstracting H atoms from the solvent rather than from protonation of R^- [equation (9)].

$$R^{\bullet} + MeCN \longrightarrow RH + {}^{\bullet}CH_2CN \qquad (9)$$

In order to account for the formation of carboxylate through the mechanism involving preceding Co–C bond breaking, intermediacy of the nucleophilic carbanion R^- as a trap for CO_2 must be considered [equation (10)]. A survey of the

$$R^- + CO_2 \longrightarrow RCO_2^- \qquad (10)$$

voltammetric peak potentials and of the standard potentials reported in Table 1, together with the electrolysis potentials of Table 3, clearly shows that, even if Co–C bond breaking is homolytic, the carbanion R^- is formed by electron transfer to the free radical $R^{\bullet}$, either at the electrode, at the applied potential [equation (8)] or in solution [equations (11) and (12)].

$$R^{\bullet} + [Co^{II}L(R)]^- \rightleftharpoons R^- + [Co^{III}L(R)] \qquad (11)$$

$$R^{\bullet} + [Co^{I}L]^- \rightleftharpoons R^- + [Co^{II}L] \qquad (12)$$

On the grounds of all the above considerations, the experimental results for compounds **3** and **4** appear to be satisfactorily accounted for assuming homolytic cleavage of the Co–C bond according to equation (5). The radical $R^{\bullet}$ thus produced partitions into two competitive reaction channels involving either H-atom abstraction, yielding the hydrocarbon, or further reduction to R^- which, interacting with CO_2, yields the carboxylate. This conclusion appears to be confirmed by the results in Table 4, showing that a shift of the electrolysis potential to more negative values, increasing the rate of R^- production, enhances the formation of carboxylate at the expense of the hydrocarbon. This last result would be more difficult to rationalise assuming that the key step of the process is direct attack of CO_2 on the reduced organometallic complex, since no effect of the applied potential is expected in that case.

According to this mechanism, CO_2 does not enter into the catalytic cycle, its role being rather to trap R^-, thus preventing the parasitic reactions which destroy the catalyst.[15] Nevertheless, electrocarboxylation can be considered as a catalytic process insofar as it takes place at a potential more positive than that of the direct two-electron reduction of the benzylic chlorides.

The fate of the $^{\bullet}CH_2CN$ radical stemming from reaction (9) requires some comments. No radical–radical coupling products, such as succinonitrile or hydrocinnamonitrile, were found in the electrolysed solutions. This is consistent with the observed charge consumption of *ca.* 2 F per mol of RCl transformed, indicating that this radical should undergo further one-electron transfer to $NCCH_2^-$. The consistent amounts of NBu^n_3 found among the electrolysis products of benzyl chloride possibly derive from a Hofmann elimination involving $NBu^n_4{}^+$ cations[21] and $NCCH_2^-$.

Considering now the electrocarboxylation of compounds **1** and **2**, the net prevalence of carboxylate over hydrocarbon (see Table 3) does not allow one to exclude any of the above mechanisms. As already indicated, the charge distribution around the Co–C bond in organometallic complexes of the type $[Co^{III}(chel)R]$ (chel is a tetradentate chelating ligand) is strongly influenced by the electron-donor property of the R moiety.[14] For high values of the latter the complex can be viewed as Co^{I}–R while Co^{II}–R^-, *i.e.*, a carbanion co-ordinated to a cobalt(II) species, is a better picture of the situation when R is a poor electron donor, the carbanionic character of the Co–C bond increasing in parallel with the electron-withdrawing ability of R.[14c,e] An inspection of the data in Table 1 shows that this latter property increases in passing from **4** to **1**, as suggested by the E° values of $R^{\bullet}$ and by the reduction peak potential of $[Co^{III}L(R)]$. The consequent increase of the carbanionic character of the Co–C bond in the organometallic intermediate would account both for a direct attack of CO_2 on the latter [equation (13)] as well as for a net prevalence of heterolytic

$$[Co^{II}L(R)]^- + CO_2 \longrightarrow [Co^{II}L] + RCO_2^- \qquad (13)$$

[equation (6)] over homolytic bond breaking. Owing to the trapping reaction (10), carboxylate would be the main expected product in both cases. Reaction (13) might involve insertion of CO_2 into the Co–C bond, with formation of the intermediate $R{-}C(O)O{-}Co^{II}L^-$, followed by Co–O bond breaking. However, owing to the carbanionic character of R, the process can be viewed as an electrophile–nucleophile interaction, concerted with Co–C bond breaking. With the data so far available it is not easy to discriminate between the various possible mechanisms.

In the presence of substantial amounts of water a remarkable decrease in the acid to hydrocarbon ratio is observed, for all the halides examined (see Table 3). The additional amount of RH produced under these conditions is attributed to protonation of R^-, at least for compounds **3** and **4** [equation (14)] and/or to

$$R^- + H_2O \longrightarrow RH + OH^- \qquad (14)$$

hydrolysis of the reduced organometallic complex [equation (15)]. Hydrolysis has been observed as one of the

$$[Co^{II}L(R)]^- + H_2O \longrightarrow [Co^{II}L] + RH + OH^- \qquad (15)$$

decomposition pathways of one-electron-reduced organocobalt complexes with tetradentate Schiff-base ligands.[14d,22] Although reaction (14) cannot be neglected, interaction of R^- with CO_2 is expected to be overwhelming with respect to proton transfer from a relatively weak acid such as water.

The hypothesis that the main effect of water addition is to promote hydrolysis (15) of the intermediate $[Co^{II}L(R)]^-$ is supported by the result of electrolysis in the presence of D_2O. The data in Table 3 indicate that toluene is the main product of benzyl chloride reduction in CO_2-saturated acetonitrile in the presence of both light and heavy water. However, when D_2O is present, 80% of toluene is deuteriated. This result can be accounted for assuming that, as under anhydrous conditions, also in the presence of 1 mol dm^{-3} water a quantity of toluene comparable with that of the carboxylate, is formed from homolytic Co–C bond cleavage [equation (5)]. A fraction of the ensuing radical $R^{\bullet}$ abstracts H atoms from the solvent, yielding toluene, in competition with its reduction to R^-, which is converted into carboxylate. The light fraction of toluene obtained by electrolysis of benzyl chloride in the presence of D_2O would be produced through this pathway while the heavy fraction would be formed through the hydrolysis (15).

It can be said, in conclusion, that, when carried out in the presence of CO_2, the electrochemical reduction of benzyl chlorides catalysed by [Co(salen)] leads to the corresponding carboxylic acids and hydrocarbons in good yields and high turnover numbers. The process involves the intermediate formation of the organometallic complex $[Co^{II}(salen)R]^-$. The relative yields of the electrolysis products are strongly influenced by the electron-donor power of the R moiety, formation of RCO_2^- being highly favoured by the presence of electron-withdrawing groups.

Acknowledgements

Financial support by the National Research Council, through the Progetto Finalizzato Chimica Fine II, is gratefully acknowledged. We thank Professor S. Daolio for the mass spectrometric analysis of electrolysis products.

References

1 G. Silvestri, in *Carbon Dioxide as Source of Carbon: Biochemical and Chemical Uses*, eds. M. Aresta and G. Forti, NATO ASI Ser. C, Reidel, Dordrecht, 1987, vol. 206, p. 339; S. Wawzonek, R. C. Duty and J. H. Wagenknecht, *J. Electrochem. Soc.*, 1964, **111**, 74; M. M. Baizer and J. L. Chruma, *J. Org. Chem.*, 1972, **37**, 1951; J. H. Wagenknecht, *J. Electroanal. Chem. Interfacial Electrochem.*, 1974, **52**, 489; D. A. Tyssee, J. H. Wagenknecht, M. M. Baizer and J. L. Chruma, *Tetrahedron Lett.*, 1972, 4809.

2 G. Silvestri, S. Gambino, G. Filardo and A. Gulotta, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 979; G. Silvestri, S. Gambino, G. Filardo, G. Greco and A. Gulotta, *Tetrahedron Lett.*, 1984, **25**, 4307.

3 O. Sock, M. Troupel and J. Perichon, *Tetrahedron Lett.*, 1985, **26**, 1509; J. Pouliquen, M. Heintz, O. Sock and M. Troupel, *J. Chem. Educ.*, 1986, **63**, 1013; M. Heintz, O. Sock, C. Saboureau, J. Perichon and M. Troupel, *Tetrahedron*, 1988, **44**, 1631.

4 S. Torii, H. Tanaka, T. Hamatani, K. Morisaki, A. Jutand, F. Pfluger and J. F. Fauvarque, *Chem. Lett.*, 1986, 169; J. F. Fauvarque, A. Jutand and M. Francois, *New J. Chem.*, 1986, **10**, 119; *J. Appl. Electrochem.*, 1988, **18**, 109; C. Amatore and A. Jutand, *J. Am. Chem. Soc.*, 1991, **113**, 2819; C. Amatore, A. Jutand, F. Khalil and F. Nielsen, *J. Am. Chem. Soc.*, 1992, **114**, 7076; K. Osaka, R. Sato and T. Yamamoto, *Organometallics*, 1994, **13**, 4645.

5 G. N. Shrauzer and E. Deutsch, *J. Am. Chem. Soc.*, 1969, **91**, 3341; D. Lexa, J. Mispelter and J. M. Savéant, *J. Am. Chem. Soc.*, 1981, **103**, 2034; A. Puxeddu and G. Costa, *J. Chem. Soc., Dalton Trans.*, 1982, 1285; G. B. Maiya, B. C. Han and K. M. Kadish, *Langmuir*, 1989, **5**, 645;

6 (*a*) D. J. Brockway, B. O. West and A. M. Bond, *J. Chem. Soc., Dalton Trans.*, 1979, 1891; (*b*) J. M. Duprilot, F. Bedioui, J. Devynck, J. C. Folest and C. Bied-Charreton, *J. Organomet. Chem.*, 1985, **286**, 77; (*c*) D. L. Zhou, O. Tinembart, R. Scheffold and L. Walder, *Helv. Chim. Acta*, 1990, **73**, 2225; (*d*) A. A. Isse, A. Gennaro and E. Vianello, *J. Chem. Soc., Dalton Trans.*, 1993, 2091.

7 D. L. Zhou, J. Gao and J. F. Rusling, *J. Am. Chem. Soc.*, 1995, **117**, 1127; A. J. Fry and U. N. Sirisoma, *J. Org. Chem.*, 1993, **58**, 4919; H. Bhandal, V. F. Patel, G. Pattenden and J. J. Russell, *J. Chem. Soc., Perkin Trans.*, 1, 1990, 2691; A. Puxeddu, G. Costa and N. Marsich, *J. Chem. Soc., Dalton Trans.*, 1980, 1489.

8 F. Bedioui, Y. Robin, J. Devynck and C. Bied-Charreton, *J. Organomet. Chem.*, 1987, **326**, 117.

9 J. C. Folest, J. M. Duprilot, J. Perichon, Y. Robin and J. Devynck, *Tetrahedron Lett.*, 1985, **26**, 2633.

10 C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, 1969, 946.

11 A. Gennaro, A. A. Isse and E. Vianello, *J. Electroanal. Chem. Interfacial Electrochem.*, 1990, **289**, 203.

12 R. I. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706; L. Nadjo and J. M. Saveant, *J. Electroanal. Chem. Interfacial Electrochem.*, 1973, **48**, 113.

13 (*a*) B. A. Sim, D. Griller and D. D. M. Wayner, *J. Am. Chem. Soc.*, 1989, **111**, 754; (*b*) B. A. Sim, P. H. Milne, D. Griller and D. D. M. Wayner, *J. Am. Chem. Soc.*, 1990, **112**, 6635; (*c*) P. Hapiot, V. V. Konovalov and J. M. Savéant, *J. Am. Chem. Soc.*, 1995, **117**, 1428.

14 (*a*) A. M. Van Den Bergen, D. J. Brockway and B. O. West, *J. Organomet. Chem.*, 1983, **249**, 205; (*b*) D. Lexa and J. M. Savéant, *J. Am. Chem. Soc.*, 1978, **100**, 3220; (*c*) G. Costa, A. Puxeddu and E. Reisenhofer, *J. Chem. Soc., Dalton Trans.*, 1972, 1519; (*d*) G. Costa, A. Puxeddu and E. Reisenhofer, *Chem. Commun.*, 1971, 993; (*e*) G. Costa, A. Puxeddu and E. Reisenhofer, *Experientia*, 1971, **18**, 235.

15 G. Costa, A. Puxeddu, C. Tavagnacco, G. Balducci and R. Kumar, *Gazz. Chim. Ital.*, 1986, **116**, 735; C. M. Elliot, E. Hershenhart, R. G. Finke and B. L. Smith, *J. Am. Chem. Soc.*, 1981, **103**, 5558; M. D. Le Hoang, Y. Robin, J. Devynk, C. Bied-Charreton and A. Gaudamer, *J. Organomet. Chem.*, 1981, **222**, 311.

16 C. Floriani and G. Fachinetti, *J. Chem. Soc., Chem. Commun.*, 1974, 615; G. Fachinetti, C. Floriani and P. F. Zanazzi, *J. Am. Chem. Soc.*, 1978, **100**, 7405; G. Fachinetti, C. Floriani, P. F. Zanazzi and A. R. Zanzari, *Inorg. Chem.*, 1979, **18**, 3469; S. Gambarotta, F. Arena, C. Floriani and P. F. Zanazzi, *J. Am. Chem. Soc.*, 1982, **104**, 5082.

17 (*a*) D. J. Pearce and D. Pletcher, *J. Electroanal. Chem. Interfacial Electrochem.*, 1986, **197**, 317; (*b*) A. A. Isse, A. Gennaro, E. Vianello and C. Floriani, *J. Mol. Catal.*, 1991, **70**, 197.

18 M. H. Schmidt, G. M. Miskelly and N. S. Lewis, *J. Am. Chem. Soc.*, 1990, **112**, 3420.

19 D. A. Koch, B. J. Henne and D. E. Bartak, *J. Electrochem. Soc.*, 1987, **134**, 3062.

20 F. M'Halla, J. Pinson and J. M. Savéant, *J. Electroanal. Chem. Interfacial Electrochem.*, 1978, **89**, 347; F. M'Halla, J. Pinson and J. M. Savéant, *J. Am. Chem. Soc.*, 1980, **102**, 4120; D. Bethell and V. D. Parker, *J. Chem. Soc., Perkin Trans. 2*, 1982, 841; G. A. Urove and D. G. Peters, *J. Electrochem. Soc.*, 1993, **140**, 932.

21 J. L. Webb, C. K. Mann and H. M. Walborsky, *J. Am. Chem. Soc.*, 1970, **92**, 2042; A. J. Fry and R. G. Reed, *J. Am. Chem. Soc.*, 1972, **94**, 8475; A. M. Romanin, A. Gennaro and E. Vianello, *J. Electroanal. Chem. Interfacial Electrochem.*, 1978, **88**, 175; G. A. Urove, D. G. Peters and Mubarak, *J. Org. Chem.*, 1992, **57**, 786.

22 P. Walder, R. Scheffold and L. Walder, *Helv. Chim. Acta*, 1992, **75**, 995; S. Shi, A. Bakac and J. Espenson, *Inorg. Chem.*, 1991, **30**, 3410.

Received 11*th August* 1995; *Paper* 5/05397H