

SOME CATHODIC ORGANIC SYNTHESSES INVOLVING CARBON DIOXIDE

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Carbon dioxide has been reduced by the dropping mercury electrode¹ and by amalgams.² In addition, it has occasionally been bubbled during reduction processes through catholytes containing aryl olefins³ and acetylene,⁴ polynuclear hydrocarbons,⁴ butadiene,^{3a,5} aromatic ketones,⁶ α,β -unsaturated aryl and aryl-substituted alkyl ketones,⁷ and benzalaniline⁸ to form carboxylic acids. Tsutsumi and Murakawa have reported the electrocarboxylation of acrylonitrile in low yield.⁹ Recently, K. S. Udupa *et al.*¹⁰ have claimed a practical synthesis of formic acid by electroreduction of CO₂. No comment was usually made in these studies concerning the question of whether electron-transfer occurred to CO₂ or to the other substrate or to both depolarizers. CO₂ is reduced in DMF or DMSO¹¹ at ca. -2.1 to -2.2 v vs. SCE.

We are reporting representative results of practical interest for synthesis, of a study of the electroreduction of solutions containing CO₂ and the following additional substrates: (a) none, (b) activated olefins, (c) nonactivated olefins, (d) aralkyl halides, (e) alkyl halides. Details concerning individual segments of this project will appear elsewhere.

CO₂ alone.—In contrast to previous work¹² which reports the reduction of CO₂ (2e⁻/2 moles) in dipolar aprotic media to CO₃⁻² and CO, we have found that the major reduction product in similar media is oxalate (Table 1).

Table 1. Electrolysis of CO₂ in DMF at Mercury^a

Current density ^b	E ^c	Moles oxalate/carbonate ^{d,e}
1	-2.0	15.0
6	-2.1	3.2
18	-2.15 to -2.2	92.0

^a Solution initially had 0.2 M Et₄NBr. ^b In ma/cm²; controlled parameter. ^c In v vs. SCE; measured but not controlled. ^d Analysis by glc of the butyl esters obtained by treating the catholyte with butyl bromide (cf., ref. 13).

^e Typical current efficiency to both products 83%.

Activated olefins.—The electrocarboxylations of activated olefins cited above have with few exceptions been restricted to the reaction of CO_2 with relatively long-lived species formed by reducing the electroactive olefin. We have examined the carboxylation of extremely short-lived electrode intermediates^{1,2} (Table 2). Preliminary experiments with methyl acrylate as the substrate have shown that the intermediate anion radical may be made to react with CO_2 /water/unreduced olefin in competition. This results in varying amounts of mono- and dicarboxylated substrate as well as dimerized substrate in which the monomer has undergone monocarboxylation. When diactivated olefins (e.g., dimethyl maleate) show two separate waves in the presence of CO_2 , product selectivity is determined by the potential at which the bulk electrolysis is run.

Table 2. Electroreduction^a of Activated Olefins + CO_2 ^b

Olefin	$-E_{1/2}$ ^c	n ^d	Products ^e	Current Efficiency (%)
$\text{CH}_2=\text{CHCOCH}_3$	1.91	2	$\text{MeOCO}(\text{CH}_2)_2\text{COCH}_3$	22
$\text{CH}_2=\text{CHCN}$	2.14	2	$\text{MeOCOCH}_2\text{CH}(\text{CN})\text{COOMe}$	41
$\text{CH}_2=\text{CHCOOMe}$	2.10	2	$\text{MeOCOCH}_2\text{CH}(\text{COOMe})_2$	52
$\text{MeOCOCH}=\text{CHCOOMe}(\text{cis-})$	1.53	1	$(\text{MeOCO})_2\text{CHCH}(\text{COOMe})_2$	46
$\text{MeOCOCH}=\text{CHCOOMe}(\text{cis-})$	1.84	2	$(\text{MeOCO})_2\text{CHCH}(\text{COOMe})_2$	31

^a $\text{CH}_3\text{CN}/0.2 \text{ M Et}_4\text{NOTs} (\text{p}^-)$, Hg cathode. ^b Olefin added slowly in course of run to catholyte through which CO_2 was bubbling. ^c Polarographically at ca. 10^{-3} M olefin and 10^{-3} M dissolved CO_2 . Cf. ref. 11. Macro-runs on waves indicated. ^d Coulometric. ^e Determined by glc after treating catholyte with MeI according to footnote d in Table 1. Product identity established by nmr, mass spectral and elemental analyses.

Nonactivated olefins.—As mentioned, CO_2 is electroreduced at ca. -2.2 v . The participation of CO_2 must therefore be considered in the reported formation of carboxylic acids from certain hydrocarbons which are more difficult to reduce than CO_2 : butadiene (-2.6), styrene (-2.45), naphthalene (-2.53), phenanthrene (-2.47).¹⁴

CO_2 must unequivocally be involved when electroinactive olefins are used. We have found that electrolysis of CO_2 at Hg in the presence of either 3,4-dihydropyran or norbornadiene results in incorporation of CO_2 : the latter olefin in $\text{Et}_4\text{NCl}-2\% \text{ H}_2\text{O}-\text{MeCN}$ is converted to

3-nortricyclenecarboxylic acid. In this connection, Norman *et al.*¹⁵ have shown that $\text{CO}_2^{\cdot-}$ and $\cdot\text{CO}_2\text{H}$, generated by H abstraction from HCOO^- and HCOOH respectively undergo typical radical addition reactions.

Alkyl halides.—We have already reported¹⁶ that reduction of benzyl halide in the presence of CO_2 leads directly to benzyl phenylacetate. Bis-halomethyl aromatics under similar conditions yield polyesters as, e.g., from *m*- and *p*-xylylene dibromide/dichloride, 4,4'-bis-chloromethylbiphenyl. Nmr analyses indicate that probably no polyhydrocarbon is formed.

Alkyl halides.—Reduction of $\text{RX}+\text{CO}_2$ at Hg yields RCOOR , R_2CO_3 , R_2Hg and oxalate (Table 3). Depending on the cathode voltage needed, R^- and/or $\text{CO}_2^{\cdot-}$ may be involved. At graphite, other types of products are formed possibly arising by attack of R^- upon the electrolyte and solvent.

Table 3. Reduction of $\text{RX}+\text{CO}_2$ in DMF/ Et_4NX

RX	Cathode	Products (%)	Substrate reduced	
			RX	CO_2
n-C ₅ H ₁₁ Br	Hg	C ₅ H ₁₁ COOC ₅ H ₁₁ (8) (C ₅ H ₁₁) ₂ CO ₃ (10) (C ₅ H ₁₁) ₂ Hg(20)	+	+
n-C ₄ H ₉ Br	Hg	(C ₄ H ₉) ₂ Hg no esters	+	-
n-C ₅ H ₁₁ Cl	Hg	C ₅ H ₁₁ COOC ₅ H ₁₁ (small) (C ₅ H ₁₁) ₂ CO ₃ (small) oxalate (major)	-	+
n-C ₄ H ₉ Br	Graphite	C ₅ H ₁₁ COOC ₅ H ₁₁ CH ₃ CH(COOC ₄ H ₉) ₂ (34) C ₄ H ₉ OCOCOMe ₂ (8) CH ₃ CHNEt ₂ (trace) COOC ₄ H ₉ n-C ₈ H ₁₈	+	-

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