Stereoselectivity and Adsorption in the Kolbe Reaction

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Summary The distribution of stereoisomeric dimers and ethers, and the dimer:alkene ratio in the products of anodic oxidation of 4-substituted cyclohexane- and cyclohexene-carboxylates strongly suggests that for saturated molecules adsorption is unimportant but that for unsaturated carboxylates it can influence the product distribution.

It is widely believed that radical intermediates involved in the Kolbe reaction are either tightly adsorbed[1] throughout the course of the reaction or that they behave[2] essentially as free radicals albeit in high concentration. The product distribution resulting from electrolysis of substituted phenyl acetates is influenced[3] by added anions and nuclear substitution in a way which implies the important adsorption of key intermediates and we report here experiments which confirm the influence on product distribution of adsorption of phenyl groups but which also strongly support the view that the radicals involved in Kolbe coupling of saturated carboxylates are essentially free.

The anodic coupling of carboxylates which are optically active by virtue of an α-chiral centre to give optically inactive products[4] is often quoted in support of free-radical intermediates but little is proved because racemisation of the radical would result whatever the position of a dynamic adsorption–desorption equilibrium and the electrode could not distinguish between the two configurations of adsorbed radicals. Coupling between conformationally biased cyclohexyl radicals allows a distinction because coupling between "free" radicals would be expected to produce a 1:2:1 mixture of the *a*:*a*, *a*:*e*, and *e*:*e* dimers whereas strong adsorption of radicals at the surface would cause distortion from this ratio.

The Table shows the products of anodic oxidation of several substituted cyclohexanecarboxylates together with the results of solvolysis experiments which might be expected to reflect the free solution behaviour of carbenium ion intermediates.

The three stereoisomers of 4,4′-di-t-butylbicyclohexyl (*a*:*a*; *a*:*e*; *e*:*e*) were identified by accurate mass measurement on samples separated by g.l.c. and were in the ratio 1:2:1. The largest component of the mixture was characterised by the inequivalence of its t-butyl groups according to ^{1}H n.m.r. spectroscopy (220 MHz). Identification of the remaining isomers followed from photochemical epimerisation[5] of the combined dimeric products which resulted in almost complete conversion into the most stable isomer (*e*:*e*).

Table

Carboxylate (or brosylate)	Concentration (mol)	Current density (A cm^{-2})[a]	Alkane (%)	Alkenes (%)	Ethers (%) *cis*	*trans*	Dimers (%) *a*:*a*	*a*:*e*	*e*:*e*	Others (%)
trans-4-t-Butylcyclohexyl[b]	0·33	0·4	19·3	32·1	3	7·5	*ca.* 6·3	*ca.* 12·6	*ca.* 6·3	12·8
								25·2		
(Brosylate methanolysis, 80°)	0·06	—	—	59·7	40·3	—		—		—
trans-4-Phenylcyclohexyl	0·33	0·4	18·9	44·4	4·2	9·0	12·3 (*ca.* 1:2:1)			11·3
(Brosylate methanolysis, 80°)	0·06	—	—	57·2	42·8	—		—		—
cis-4-Phenylcyclohex-2-enyl	1·0[c]	0·5	—	8·8[d]	(Δ¹-3-MeO-4-Ph) 7·2	19·0	11·2[e]			4·6
					(Δ¹-3-Ph-6-MeO) 29·8	19·3				
″ ″ ″	1·8	0·5	—	7·6	37·4		44·9[e]			10·2
trans-4-t-Butylcyclohexyl acetate ion	0·14 0·14	0·03	7·0	<1·0	60·5[f]		29·5[g]			2·0

[a] Undivided cell, Pt electrodes, 20% neutralised with NaOMe, 2F mol^{-1}; [b] Similar results were obtained from the *cis* isomer; [c] 50% neutralised; [d] Phenylcyclohexenes and diphenyl (2·9%); [e] At least 7 isomers; [f] Water present therefore alcohols, ethers, and ketone present; [g] Bicyclohexyls (7·5%, ratio 1:2:1), 4-methyl-t-butylcyclohexane(22·0%; *cis*:*trans* 1:1).

The cyclohexyl radicals involved in Kolbe electrolysis of 4-t-butylcyclohexanecarboxylates combine, therefore, in a random fashion which strongly suggests that adsorption at the anode is weak or unimportant for coupling. Random coupling is also observed in the crossed Kolbe reaction involving acetate ion (Table).

The *distribution* of the products of electrolysis of *trans*-4-phenylcyclohexanecarboxylates and *cis*-4-phenylcyclohex-2-enecarboxylates suggests that for unsaturated carboxylates the intermediates may be adsorbed at the anode. For the cyclohexane system, 4-phenyl substitution causes, relative to the t-butyl compound, a decrease in dimer formation with a concomitant increase in alkene formation. Methanolysis of the relevant 4-phenyl and 4-t-butyl brosylates results in similar substitution:elimination ratios, which implies that the bulk solution behaviour of the carbenium ions would be similar. It is improbable for steric reasons that in solvolysis the ethers arise *via* S_N2 attack or the alkene by an $E2$ mechanism.[6]

The adsorption of aromatic molecules at anodes is well known[7] and is the basis of rationalisation of products formed in the anodic oxidation of aromatic hydrocarbons.[8] For the cyclohexanecarboxylates such enhancement of adsorption would, at the potentials of the Kolbe reaction, facilitate further anodic oxidation to the carbenium ion thus increasing alkene formation at the expense of radical combination. Alternatively, adsorption might in some unknown way cause disproportionation to be favoured over combination.

An equilibrium distribution of ethers comes from electrolysis of the saturated carboxylates (Table). The four ethers formed by anodic oxidation of *cis*-4-phenylcyclohex-2-enecarboxylate are derived from the allylic carbenium ion and the *cis*-1-ether is the largest single substitution product even though it is probably not the most stable. The inference is that the carbenium ion is reacting whilst still held at the electrode surface.

Of the nine isomeric dimers which would arise from Kolbe coupling of *cis*-4-phenylcyclohex-2-enecarboxylate seven have been resolved in the gas chromatogram and identified by accurate mass measurements on their molecular ions. The stereochemical characterisation of the individual dimers is not yet complete but the areas of the seven g.l.c. peaks (3:1:6:6:4:5:2·5) suggests that in this case coupling is not random because the nine dimers would thereby be formed in the ratio 1:2:1:2:4:2:1:2:1. This result is also consistent with the more likely involvement of unsaturated groups in adsorption at anodes.

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