Anodic Oxidation of Phenylacetate Ions

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Summary The major factors influencing the competition between radical and carbonium ion pathways have been assessed for the anodic oxidation of substituted phenylacetate ions at platinum: the distribution of products, and the effect of added perchlorate ion, can be rationalised in terms of a scheme which involves the adsorption of key intermediates, and from which expressions may be derived relating product distribution with structural, electrochemical, and adsorption parameters.

The anodic oxidation of carboxylates has long been known to give products derived from both radicals and carbonium ions,[1] but no systematic study of the competition, in one chemical system, has previously been reported.

Product analyses following electrolysis of phenylacetate are summarised in Figure 1 together with the total current efficiency. The predominance of benzaldehyde formation at low current density was unexpected and is attributed to reaction between benzyl radicals and oxygen.[2] It cannot result from further anodic oxidation of benzyl methyl ether to the dimethyl acetal with subsequent hydrolysis (overall a 4e process)[3] as this would imply current efficiency *ca.* 150%. Furthermore, we found that under the conditions used the dimethyl acetal was not hydrolysed.

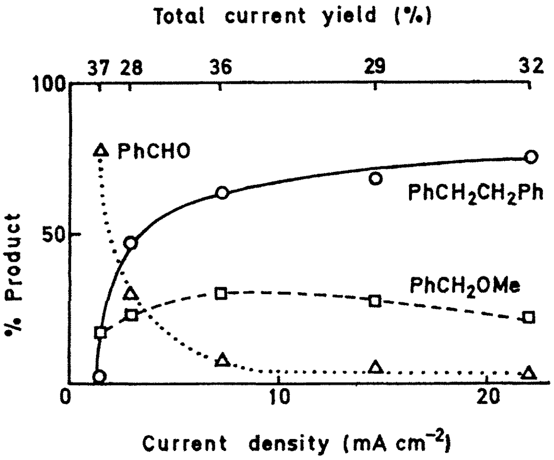


Figure 1. *Electrolysis of* $PhCH_2CO_2H$ (0·5m) *and* $PhCH_2CO_2Na$ (0·5m) *in methanol. Analysis after* 0·05 F mol^{-1}.

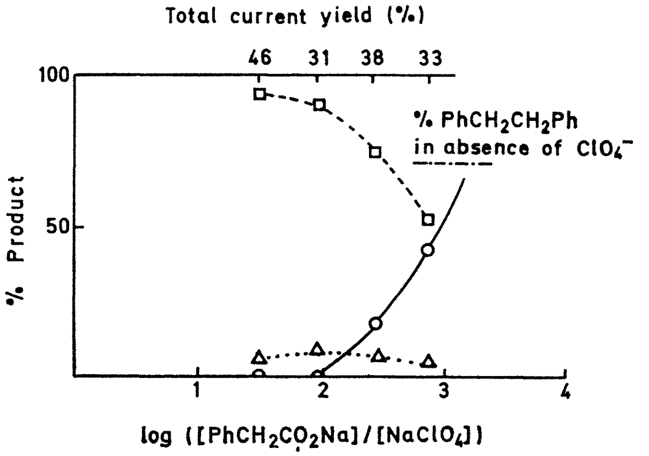


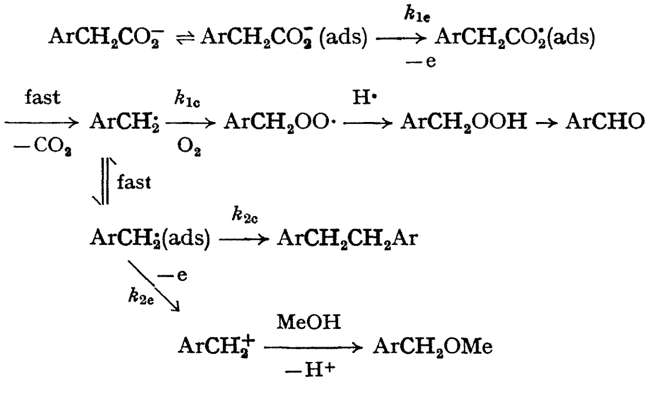
Figure 2. *Electrolysis of* $PhCH_2CO_2H$ (0·5m) *and* $PhCH_2CO_2Na$ (0·5m) *at* 14·7 mA cm^{-2} *with added* $NaClO_4$. *Analyses after* 0·05 F mol^{-1}.

The effect of the addition of relatively small proportions of other anions is pronounced. The addition of only one-hundredth molar proportion of perchlorate (relative to the acetate ion) completely suppresses formation of the Kolbe dimer (Figure 2). In the absence of added ions, electrolysis of nuclear substituted phenylacetates at fixed current density reveals that polar and steric effects also influence the competition (Table). Mesomerically electron-donating substituents lead to high yields of carbonium ion products whereas the best yield of coupled product is obtained from the acid containing the electron-withdrawing pentafluorophenyl group. For a given substituent the *ortho* isomer gives higher proportions of the carbonium ion product and *para* substitution by the bulky t-butyl group also favours further oxidation to the cation. Methoxy substituted aromatic compounds are easily oxidised by direct electron transfer from the nucleus[4] and it is possible that *p*-methoxyphenylacetic acid is oxidised by such a route. The particularly low anode potential for this electrolysis supports such a view.

Electrolysis of substituted phenylacetic acids[a]

Substituent	$(ArCH_2-)_2$	Product analysis[b] $ArCH_2OMe$	ArCHO	Others	Anode potential V *vs.* S.C.E.
F_5	74	7	14	5	2·11—2·30
H	68	13	8	11	2·50—2·43
p-CF_3	37	18	24	21[c]	1·90—1·94
m-Me	40	32	12	16	2·18—2·20
m-CF_3	30	26	20	24[c]	1·85—1·92
p-Me	38	46	8	8	2·20—2·32
o-CF_3	24	34	21	21[c]	1·97—2·02
o-Me	14	66	10	10	1·85—2·02
p-Bu^t	13	78	—	9	1·79—1·91
p-Cl	4	91	—	5	2·10—2·06
p-F	<1	90	—	10	1·86—2·00
p-OMe	<1	99	—	<1	1·39—1·40

[a] Current density 14·7 mA cm^{-2}. Acid, 0·02 mol, 50% neutralised in methanol (20 ml), pyridine (5 ml). [b] Peak area %. Analyses after 0·05 F mol^{-1}. [c] Several minor components, individually less than 10%.



SCHEME

We rationalise our results in the Scheme which also depicts the probably important role of adsorption. From this scheme, and using the steady state approximation for the concentration of benzyl radicals at the anode surface, combined with simple expressions for electrochemical rates,[5] we have derived equation (1) for the relative extent of dimerisation and benzyl cation formation.

$$[ArCH_2)_2]/[ArCH_2^+] = \left(\tfrac{1}{4} + \frac{k_{2c}k_{1e}(C_a)_s(1-\theta)}{[k_{2e}(1-\gamma)]^2[1+\exp(\Delta G^r_{ads}/\boldsymbol{R}T)]}\right)^{\frac{1}{2}} - \tfrac{1}{2} \qquad (1)$$

The parameters k_{1e} and k_{2e} are potential dependent electrochemical rate coefficients, k_{2c} is a chemical rate coefficient, $(C_a)_s$ is the concentration of arylacetate ions at the surface, θ is the fractional coverage by anions, γ the fractional coverage by benzyl radicals, and ΔG^r_{ads} the standard free energy of adsorption of the benzyl radicals.

A similar expression [equation (2)] describes the relative extent of dimerisation and reaction with oxygen.

$$[(ArCH_2)_2]/[ArCH_2O_2\cdot] = \left(\tfrac{1}{4} + \frac{k_{2c}k_{1e}(C_a)_s(1-\theta)}{[k_{1c}\exp(\Delta G^r_{ads}/\boldsymbol{R}T)(O_2)]^2[1+\exp(\Delta G^r_{ads}/\boldsymbol{R}T)]}\right)^{\frac{1}{2}} - \tfrac{1}{2} \qquad (2)$$

The role of the factors discussed can be identified in these expressions. For instance added perchlorate ion would by preferential adsorption increase θ in equation (1), steric hindrance would be reflected in low value for γ and ΔG^r_{ads} and nuclear substitution would by polar effects influence k_2e and possibly ΔG^r_{ads}. The variations in product distribution as these parameters are altered is completely consistent with the above treatment.

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