Electro-organic Reactions. Part II.† Mechanism of the Kolbe Electrolysis of Substituted Phenylacetate Ions

By **James P. Coleman, Robert Lines, James H. P. Utley,*** and **Basil C. L. Weedon,** Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

For the anodic oxidation of phenylacetate and substituted phenylacetate ions changes in the distribution of products have been related to changes in electrochemical parameters, nuclear substitution, and the concentration of added perchlorate ions. The results support a reaction mechanism which involves the important adsorption of carboxylate ions and according to which added anions and bulky substituents cause surface effects which significantly effect the competition between radical and carbenium ion pathways. For *p*-methoxyphenylacetate ions oxidation is probably initiated by electron transfer from the aromatic nucleus (pseudo-Kolbe reaction). From a steady state kinetic analysis expressions have been derived which relate product distribution with structural, electrochemical, and adsorption parameters.

THE competition between one- and two-electron oxidation of carboxylates often leads to the formation of mixtures of many products which diminishes the preparative usefulness of the Kolbe reaction. Much is known[1] about the gross features of the reaction conditions and the structures of carboxylates which optimise either radical derived products (one-electron oxidation) or carbenium ion derived products (two-electron oxidation). For instance it is supposed that high current density and/or high anode potential favour one-electron oxidation and dimer formation whereas low current density, α-substitution of the carboxylate with electron-donating substituents, and the presence of foreign anions are all features which are known to favour two-electron oxidation to carbenium ions. However, a systematic study of the competition between one- and two-electron oxidation, in one chemical system, has not previously been reported. In this paper we report on such a study of the oxidation of substituted phenylacetate ions. Some of the results of this work have been communicated[2] in an abbreviated form.

The main advantages of arylacetates as substrates for such a study are the relative simplicity of the product mixtures (disproportionation and elimination reactions of the benzylic intermediates are precluded) and the gradual changes in polar effects which may be introduced by remote, nuclear substitution. The products of one- and two-electron oxidation are formed in similar amounts from the unsubstituted phenylacetate which is therefore a convenient reference compound in the series. Earlier investigations[3] involving the oxidation of phenylacetate ions have not exploited these advantages to obtain generally useful mechanistic information on the Kolbe reaction.

RESULTS AND DISCUSSION

Scheme 1 contains the probable reaction paths for the anodic oxidation of arylacetate ions and forms a convenient basis for discussion of our results. The discussion will be concerned mainly with that part of the scheme initiated by oxidation according to route (3). However, the relevance of pathways (1) and (2), which involve direct oxidation of the aromatic nucleus, must be considered.

The Pseudo-Kolbe Reaction [*Scheme* 1, *Routes* (1) *and* (2)].—Arylacetates contain two electro-active centres, the carboxylate function and the aromatic nucleus. Our original suggestion[2] of the likely importance of routes (1) and (2) was based on the low anode potential required for the oxidation of *p*-methoxyphenylacetate (Table 4). Subsequently a comparison[4] of the oxidation peak potentials in cyclic voltammograms of 10-methylanthracen-9-ylacetate and triphenylacetate ions showed that the former probably oxidises anodically *via* electron removal from the aromatic nucleus. Preparative scale electrolysis of the anthracene derivative in tetrahydrofuran–methanol solution gave[4] both dimer and methyl ether, the two products expected from route (2), but the result does not preclude the participation of route (1).

Substituent effects on the oxidation peak potentials of aryl-substituted acetates are significant which implies that electron removal from the aromatic nucleus may be concerted with decarboxylation. It will be necessary to return to the above considerations in the discussion of the results of electrolysis of arylacetates containing electron-donating substituents.

Oxidation of Phenylacetate Ions.—(i) *Constant current density*. The results of oxidation at constant current density are given in Table 1. In addition to the three major products benzyl alcohol was a minor product (*ca.* 10%) in all of the phenylacetate electrolyses. This could arise from reaction between benzyl cation and adventitious amounts of water or from the decomposition of benzyl hydroperoxide (see below).

The origin of the benzaldehyde is important if a comparison between 1e and 2e products is to be attempted. Benzaldehyde could result from further 2e oxidaton of benzyl methyl ether making an overall 4e oxidation.[5] However, this would imply its formation at low current density with an improbable current efficiency of *ca.* 150%. Furthermore, benzaldehyde was not produced

---

† Part I, ref. 17.

[1] L. Eberson, ' Chemistry of the Carboxylic Acid Group,' ed. S. Patai, Interscience, London, 1970.

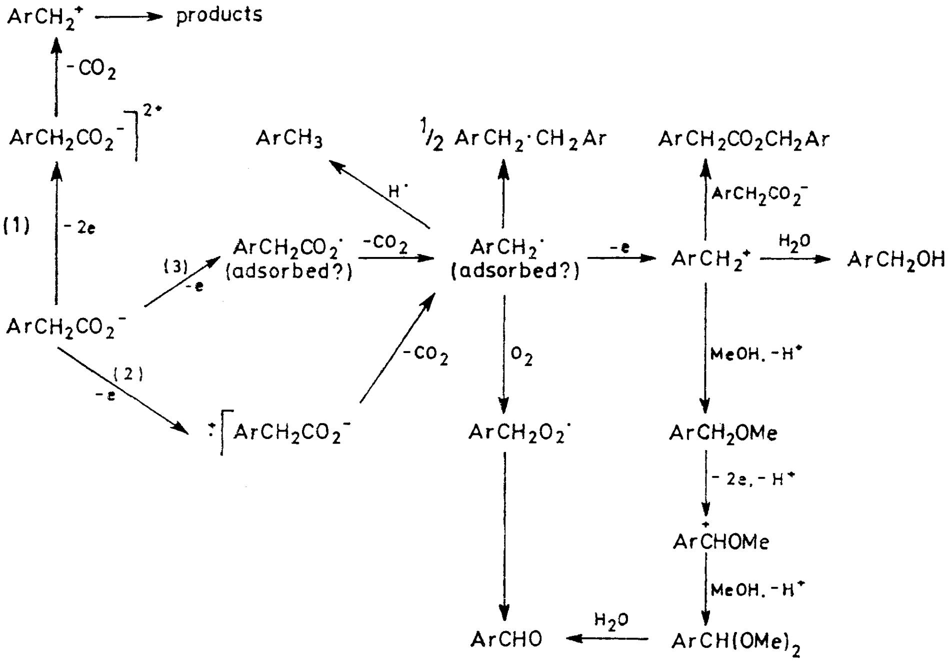
[2] J. P. Coleman, J. H. P. Utley, and B. C. L. Weedon, *Chem. Comm.*, 1971, 438.

[3] B. Wladislaw and H. Viertler, *J. Chem. Soc.* (*B*), 1968, 576; S. D. Ross and M. Finkelstein, *J. Org. Chem.*, 1969, **34**, 2923.

[4] J. P. Coleman and L. Eberson, *Chem. Comm.*, 1971, 1300.

[5] R. F. Garwood, Naser-ud-din, and B. C. L. Weedon, *Chem. Comm.*, 1968, 923.

from the corresponding dimethyl acetal in the conditions used for electrolysis and the subsequent work-up (see Experimental section). The dimethyl acetal would be the first-formed product in the 4e process. We favour, therefore, the probability that benzaldehyde is a 1e product arising from reaction between benzyl radicals and oxygen. Benzyl hydroperoxide has been shown[6] to decompose to a mixture of benzaldehyde and benzyl alcohol when catalysed by Co^{II} or Co^{III} species in acetic acid. The oxygen involved could be either dissolved or produced electrochemically from hydroxide ion. It has been shown that at low current densities, where benzaldehyde formation is important, both hydroxide and carboxylate oxidation take place and ‘ peroxides ’ have been detected in such conditions.[7] It is also consistent that peroxide formation would be favoured at low concentrations of benzyl radicals, *i.e.* before the competing bimolecular combination became significant.



SCHEME 1

TABLE 1

Constant current electrolysis of $PhCH_2CO_2H$ (0·5M) and $PhCH_2CO_2Na$ (0·5M) in methanol

Current density (mA cm^{-2}) [a]	Product analysis (%) [b]			Total current yield (%) [c]
	$(PhCH_2)_2$	$PhCH_2OMe$	PhCHO	
3·2	2	17	81	37
6·4	47	23	30	28
16·0	63	30	7	36
32·0	68	27	5	29
48·0	75	22	3	32

[a] Assumes reaction at one face of electrode only. [b] Relative peak area %, the listed components account for >90% of the total. The most abundant minor product was benzyl alcohol. [c] Calculated as $(PhCH_2)_2$ and $PhCH_2OCH_3$ 2 F mol^{-1}; PhCHO 1 F mol^{-1}.

A consequence of varying current density is that the anode potential also varies and for the conditions described in Table 1 the initial anode potential varies in the range *ca.* 2·6 V (*vs* s.c.e.) at low current density to *ca.* 2·9 V at high current density. The variations in product distribution cannot therefore be assigned solely to changes in current density unless either potential or current density can be varied independently.

(ii) *Constant potential.* By plotting voltammetric curves for phenylacetate solutions of various concentrations it proved possible to select conditions where electrolysis of the separate solutions at fixed current density required different anode potentials. Product analysis was carried out after the passage of only 0·025 F mol^{-1} (for 1e oxidation) which means that the monitored anode potentials held steady throughout the run. The shapes of the voltammetric curves were such that significant differences of anode potential could only be obtained at a relatively low current density. The results are summarised in Table 2.

It is noteworthy that at low current density there is little potential dependence of the product distribution from which it must be concluded that unless bulk solution concentration of carboxylate is important in its own right current density is the product-determining factor.

(iii) *Added perchlorate ion.* It has long been known[8] that added anions promote carbenium ion formation

---

[6] Y. Takegami, Y. Fujimura, H. Ishii, and T. Iwamota, *Kogyo Kagaku Zasshi*, 1965, **68**, 196 (*Chem. Abs.*, 1965, **63**, 14,663).

[7] M. Fleischmann, J. R. Mansfield, and Lord Wynne-Jones, *J. Electroanalyt. Chem.*, 1965, **10**, 522.

[8] H. Hofer and M. Moest, *Annalen*, 1902, **323**, 284.

from carboxylate oxidation. Yet again, however, there has been little systematic study and no explanation of the effect. To this end we have tried to quantify the effect, choosing perchlorate anion as a suitable additive which will not oxidise significantly during electrolysis.

Table 3 shows the effect of perchlorate ion on product distribution. The addition of only a one-hundredth molar proportion of perchlorate (relative to the acetate ion) completely suppresses formation of the Kolbe dimer. The small variation in the current efficiency shows that there is a real diversion of mechanism and not suppression of formation of one of the products. It is also noteworthy that the addition of perchlorate does not alter in a regular manner the anode potential in the series of constant current runs although the effective anode potential at the surface may be lower than that measured *vs.* bulk solution.

The relatively small proportion of anion needed to produce such marked variations in product distribution points to the operation of a surface effect and, because perchlorate is not oxidised at the potentials used, it is probable that specific adsorption is involved. This point is discussed further below.

TABLE 2

Controlled potential electrolysis [a] of $PhCH_2CO_2^-$ in methanol

$[PhCH_2CO_2H]$ (M) [b]	Anode potential (V *vs.* s.c.e.)	Product analysis (%) [c]			
		$(PhCH_2)_2$	$PhCH_2OMe$	$PhCH_2OH$	PhCHO
0·8	2·50	Trace	13·9	9·6	76·4
0·4	2·62	3·7	7·9	14·6	73·9
0·3	2·71	3·3	3·3	17·5	73·2

[a] Current density, 2·4 mA cm^{-1}. [b] 50% Neutralised with NaOMe. [c] Mole %.

TABLE 3

Electrolysis [a] of $PhCH_2CO_2H$ (0·5M) and $PhCH_2CO_2Na$ (0·5M) in methanol, with added sodium perchlorate

$[NaClO_4]$ (mM)	Product analysis (%) [b]			Current yield (%) [c]	Anode potential [d] (V *vs.* s.c.e.)
	$(PhCH_2)_2$	$PhCH_2OMe$	PhCHO		
0	68	27	5	29	2·5—2·6
0·65	42	53	5	33	2·4
1·77	18	75	7	38	2·4
5·18	0	91	9	31	2·35
15·80	0	94	6	46	2·2

[a] Constant current density, 32 mA cm^{-1}. [b,c] As for Table 1. [d] Monitored at end of run.

TABLE 4

Electrolysis of substituted phenylacetate ions [a]

Substituent	Product analysis (%) [b]			Others (%)	Anode potential (V *vs.* s.c.e.)
	$(ArCH_2)_2$	$ArCH_2OMe$	ArCHO		
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 32 mA cm^{-2}. 0·02M Acid, 50% neutralised in methanol (20 ml). [b] Peak area %. Analyses after 0·05 F mol^{-1}. [c] Several minor components, individually <10%.

Oxidation of Nuclear Substituted Phenylacetate Ions.— The effect of remote nuclear substitution was studied in the initial belief that the 1e : 2e product ratio would be affected in a manner easily predictable from the electron-donating or -withdrawing properties of the substituent, *e.g.* 2e oxidation should invariably be encouraged by electron-donating substituents. The correlation is much less direct than expected and the relevant results are summarised in Table 4. The substituents are arranged in order of the amount of products believed to be formed *via* radicals (1e oxidation). As expected mesomerically electron-donating substituents lead to high yields of carbenium ion products and the gross dependence on the ease of oxidation of the benzyl radical of the ratio of radical to carbenium ion derived products is further supported by the correlation [9] between the gas-phase ionisation potentials of substituted benzyl radicals and yields obtained from the Kolbe electrolysis (Table 5). The two sets of figures in Table 5 show similar trends but there is a significant deviation in the cases of the *p*-chloro- and *p*-fluoro-substituted compounds. The ionisation potentials for the *p*-chloro- and *p*-fluoro-benzyl

[9] A. Streitweiser, jun., *Progr. Phys. Org. Chem.*, 1963, **1**, 1.

radicals are greater than for the unsubstituted benzyl radical. However, in the electrolysis, the radical reaction is virtually suppressed. Mesomeric stabilisation of the carbenium ion is obviously more important than destabilisation by the inductive effect and with five ring fluorine atoms the extent of 1e oxidation just exceeded that observed for the parent phenylacetate ion. There is precedent[10] for such behaviour in the relative stabilities in aqueous sulphuric acid of a series of triphenylmethyl cations which fall into the order: $(p\text{-}FC_6H_4)_3C^+ > (C_6H_5)_3C^+ > (C_6F_5)_3C^+$.

TABLE 5

Benzyl radical ionisation potentials and Kolbe products

Substituent	Radical product (%) [a]	Ionisation potential (eV) [b]
F_5	88	
H	76	7·76
p-CF_3	61	
m-CH_3	52	7·65
m-CF_3	50	
p-CH_3	46	7·46
o-CF_3	45	
o-CH_3	24	7·61
p-Bu^t	13	*ca.* 7·4 [c]
p-Cl	4	7·95
p-F	<1	7·78
p-OCH_3	<1	6·82

[a] Dimer + aldehyde. [b] Ref. 9. [c] Estimated from results for p-CH_3 (7·46) and p-Pr^i (7·42).

Apart from the gross substituent effects it is evident that relative to hydrogen almost any substituent encourages benzyl cation formation (2e) and discourages dimer and aldehyde formation (1e).

For a given substituent, of whichever polarity, 2e oxidation is favoured by *ortho*-substitution which implies ~~the~~ important incursion of a steric effect. This conclusion is supported by a consideration of the relative effects, from the *para*-position, of methyl and t-butyl. In solvolysis reactions of benzyl derivatives the cationic transition state is stabilised more by p-methyl than by p-t-butyl substitution, *i.e.* the Baker–Nathan order is observed. The ionisation potential data would suggest, for the gas phase, a near equality of polar effect. In the anodic oxidation of benzyl radicals, however, p-t-butyl behaves as though it were more electron donating than methyl. It is highly probable that this is a consequence of the relatively large bulk of the t-butyl group and not a reversal of the expected order of polarity.

In the light of the evidence for the pseudo-Kolbe reaction (see above) the result concerning p-methoxyphenylacetate (Table 4) needs special comment. For the maintenance of a given current density, under otherwise identical conditions, the electrolysis of p-methoxyphenylacetate proceeds at a much lower potential than for other members of the series. Coleman and Eberson[4] also found that for cyclic voltammetry in acetonitrile the oxidation peak potential of caesium p-methoxyphenylacetate [1·04 V (*vs.* s.c.e.)] was markedly lower than that for caesium phenylacetate (1·43 V). A large concentration of perchlorate ion was present for the cyclic voltammetric experiments although from the present work this does not seem greatly to reduce the electrode potentials (Table **3**).

The low electrode potential can be interpreted as the result of electron-removal from the nucleus [Scheme 1, route (1) or (2)] or in terms of a large substituent effect on electron removal from the carboxylate group. The former explanation is preferable because, using the method described above, we find that at a given current density the products of electrolysis of p-methoxyphenylacetate are highly potential dependent (Table 6). This is contrary to the finding for phenylacetate (Table 2). In the electrolyses featured in Table 6 product analysis was carried out after only *ca.* 5% conversion (for 1e oxidation) and it is unlikely that the p-anisaldehyde is formed by further (2e) oxidation of the ether. The required intermediate, p-anisaldehyde dimethyl acetal, would, however, be hydrolysed much more rapidly[11] than for the benzaldehyde case. At least part of the evidence against ether oxidation, presented for the unsubstituted case, may not therefore apply here.

TABLE 6

Controlled potential electrolysis [a] of p-$MeOC_6H_4CH_2CO_2^-$ in methanol

$[p\text{-}MeOC_6H_4CH_2CO_2H]$ (M) [b]	Anode potential (V *vs.* s.c.e.)	Product analysis (%) [c]	
		$ArCH_2OMe$	ArCHO
0·8	2·04	60·7	39·3
0·4	2·14	55·0	45·0
0·2	2·30	6·7	93·3

[a] Current density, 7·1 mA cm^{-1}. [b, c] As for Table 2.

With this qualification it is highly probable that p-anisaldehyde is formed by 1e oxidation. It is the major product at 2·3 V (*vs.* s.c.e.) whereas at 2·0 V anisyl methyl ether predominates (Table 6). This result is consistent with a competition between carboxylate ion discharge and nuclear discharge with carboxylate ion discharge becoming predominant at the higher anode potential. This concept is in agreement with results for aliphatic carboxylates, the discharge of which at high potentials completely suppresses other processes, *e.g.* oxygen evolution, which normally require lower potentials.[12] Such a view implies that at low potentials the benzyl radical is formed directly at the anode and is thereby set up for further oxidation whereas at high potentials it is perpendicular to and some distance from the anode (*cf.* Figure).

Competition Between One and Two-electron Oxidation. Steady State Kinetic Analysis.—Assuming that nuclear discharge is important only for the p-methoxy-derivative, and accepting that surface effects are important because of the effect of perchlorate ion and the bulk of substituents, the reaction scheme may

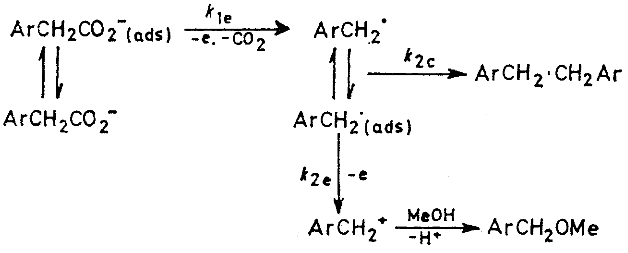
---

[10] R. Filler, C. S. Wang, M. A. McKinney, and F. N. Miller, *J. Amer. Chem. Soc.*, 1967, **89**, 1026.

[11] T. H. Fife and L. K. Jao, *J. Org. Chem.*, 1965, **30**, 1492.

[12] T. Dickinson and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, 1962, **58**, 382.

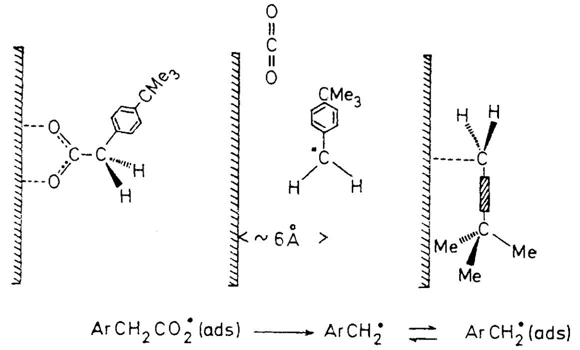
be redrawn to serve as the basis for a steady state kinetic analysis (Scheme 2). Because aldehyde formation is insignificant at all but low current densities the reaction between benzyl radicals and oxygen is omitted.



SCHEME 2

In Scheme 2 k_{1e} and k_{2e} are potential dependent electrochemical rate constants and k_{2c} is a chemical rate constant. Using the scheme and Conway's equations, conventions, and symbols,[13] expressions may be derived for the rates of formation of the various intermediates and products. Thus, $d(C_r)_s/dt = k_{1e}(C_a)_s(1 - \theta)/[1 + \exp(\Delta G^r{}_{ads}/RT)]$ where $(C_r)_s$ is the surface concentration of benzyl radicals, $(C_a)_s$ is the surface concentration of arylacetate ions, θ is the fractional coverage by anions, and $\Delta G^r{}_{ads}$ is the standard free energy of adsorption of the benzyl radicals. Similarly, $d[(PhCH_2)_2]/dt = k_{2c}(C_r)_s{}^2$ and $d(PhCH_2{}^+)dt = k_{2e}(C_r)_s(1 - \gamma)$ where γ is the fractional coverage by benzyl radicals.

An assumption that arylacetate ions and benzyl radicals do not compete for the same sites is contained in the use of separate $(1 - \theta)$ and $(1 - \gamma)$ terms rather than a $(1 - \theta - \gamma)$ term. The justification for this assumption is that following carboxylate discharge [involving $(1 - \theta)$] decarboxylation leaves a temporarily 'free' radical which is then involved in a rapidly established and new adsorption–desorption equilibrium [involving $(1 - \gamma)$]. The radical would not be so far from the surface that competition from carboxylate ion discharge would be effective and the process can probably be viewed as a reorientation with the benzyl radical being specifically adsorbed according to the Figure. On this model the original site is not reserved for the benzyl radical because the steric requirements of the adsorbed species change significantly. Thus the appropriate fractional coverage term changes from θ to γ. This view accommodates the observed effect of a bulky substituent (t-butyl) at the *para*-position.



Probable reorientation of adsorbed species at anode

There is independent evidence[14] that immediately following decarboxylation the radicals are separated from the electrode, probably by *ca.* 6 Å. It is also known that radicals derived from saturated carboxylates dimerise away from the surface but that reaction at the surface becomes more important with the introduction of unsaturation.[15] Furthermore, for aromatic hydrocarbons at gold anodes interactions of the order of 10 kcal mol^{-1} have been measured and such molecules tend to adsorb parallel to the electrode surface.[16]

Using Scheme 2 and the equations set out above the rates of formation and disappearance of the benzyl radicals may be equated and the resulting quadratic equation solved to give an expression for $(C_r)_s$. This expression may then be deployed to give equation (1) for the relative extent of dimerisation and benzyl cation formation.* The exact potential dependence of k_{1e} and k_{2e} is not known but qualitative effects can be predicted from the above expression and the role of the factors discussed in previous sections can be identified. Added perchlorate ion would, by preferential adsorption, increase θ, steric hindrance would be reflected in low values for γ and $\Delta G^r{}_{ads}$, and nuclear substitution would, by polar effects, influence k_{2e} and possibly $\Delta G^r{}_{ads}$. The observed variations in product distribution as these parameters are altered are therefore completely consistent with the above treatment.

$$[(ArCH_2)_2]/[ArCH_2{}^+] = \left(\frac{1}{4} + \frac{k_{2c}k_{1e}(C_a)_s(1 - \theta)}{[k_{2e}(1 - \gamma)]^2[1 + \exp(\Delta G^r{}_{ads}/RT)]}\right)^{\frac{1}{2}} - \frac{1}{2} \quad (1)$$

EXPERIMENTAL

Materials.—The substituted phenylacetic acids were obtained commercially, by minor modification of literature methods, or according to methods described previously.[17]

Electrolyses.—The cell and electronic equipment used has been described.[17] A typical electrolysis was as follows. The substituted phenylacetic acid (0·01 mol) and its sodium or potassium salt (0·01 mol) were dissolved in a mixture of methanol (20 ml) and redistilled pyridine (5 ml). The solution was electrolysed between two platinum plate electrodes (12·5 mm × 12·5 mm) at a constant current of 50 mA for 32 min (0·05 F mol^{-1}). The anode potential was monitored during the last 2 min of each electrolysis. Solvent was removed on a rotary evaporator, and dilute hydrochloric acid (75 ml) was added. The mixture was

---

* Dimerisation of adsorbed radicals is assumed here. It may easily be shown that multiplication by $\exp(\Delta G^r{}_{ads}/RT)$ gives the corresponding expression for dimerisation of 'free' radicals. Hence a large, negative free energy adsorption lowers the ratio of radical : cation-derived products.

[13] B. E. Conway, 'Theory and Principles of Electrode Processes,' Ronald Press, New York, 1965, p. 92.

[14] L. Eberson, *Acta Chem. Scand.*, 1963, **17**, 1196; D. L. Muck and E. R. Wilson, *J. Electrochem. Soc.*, 1970, **117**, 1358.

[15] G. E. Hawkes, J. H. P. Utley, and G. B. Yates, *J.C.S. Chem. Comm.*, 1973, 305.

[16] H. Dahms and M. Green, *J. Electrochem. Soc.*, 1963, **110**, 1075.

[17] J. P. Coleman, Naser-ud-din, L. Eberson, H. G. Gilde, J. H. P. Utley, and B. C. L. Weedon, *J.C.S. Perkin II*, 1973, 1905.

shaken with ether (2 × 60 ml) and the combined ether extract was washed with sodium hydroxide solution (2 × 35 ml; 5%), water (50 ml), dried ($MgSO_4$), filtered, and evaporated. The residue was dissolved in ether (*ca.* 1 ml) and the solution was analysed by g.l.c. The unchanged substituted phenylacetic acid was recovered by acidification of the sodium salt.

Analytical Procedures.—These have been described previously.[17]

Stability of Benzaldehyde Dimethyl Acetal.—Benzaldehyde dimethyl acetal (0·1 g) was added to phenylacetic acid (1·4 g) and sodium phenylacetate (1·6 g) in methanol (20 ml). The mixture was left at room temperature for 2 h. Methanol was removed on a rotory evaporator, and sodium hydroxide solution (50 ml; 5%) was added. The mixture was shaken with ether (2 × 60 ml) and the combined ether extract was washed with water (50 ml), dried ($MgSO_4$), filtered, and evaporated to leave a liquid residue (0·07 g). G.l.c. analysis of the crude product showed only one component, corresponding to benzaldehyde dimethyl acetal. A sample of the crude product, with benzaldehyde added, showed a new peak, t_R 5 min.

Two of us (J. P. C. and R. L.) thank the S.R.C. for research studentships.

[3/2132 *Received*, 18*th October*, 1973]