Anodic Oxidation Pathways of Arylacetate Ions; the Pseudo-Kolbe Reaction

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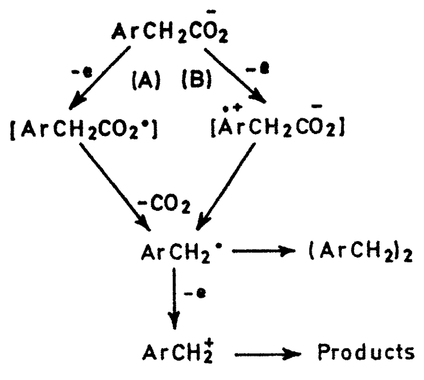
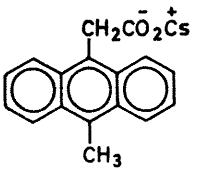
Summary Anodic oxidation of the caesium salt of 9-methylanthracene-10-acetic acid (I), to give "Kolbe" products, proceeds *via* electron removal from the aromatic nucleus.

ARYLACETATE ions can, in theory, be oxidised according to two formally distinct pathways,[1] namely by electron removal from the carboxylate group [(A), the normal Kolbe reaction mechanism] or the aryl group [(B), denoted the *pseudo*-Kolbe reaction]:

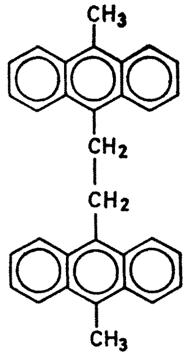


SCHEME

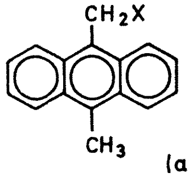
Since the CO_2 molecule lost in the decarboxylation step is thought to play an important role in determining the course of the Kolbe reaction (stereochemistry,[2a] radical *versus* cation pathway[2b]), it should be possible to design arylacetate ions where the site of oxidation is the aryl group instead of the carboxylate ion, thereby obtaining a new tool for the understanding of this complex reaction.[2c] We report one case of such an oxidation mechanism which we denote the *pseudo*-Kolbe reaction.



(I)



(II)



(III)

(a) X = $-OCH_3$
(b) X = $-\overset{+}{N}\equiv C-CH_3$
(c) X = $\overset{+}{N}C_5H_5$

TABLE 1

Voltammetric peak potentials, E_p, (v) versus SCE[a]

R	RH	RCO_2H	$RCO_2^-Cs^+$
9-Methyl-10-anthrylmethyl	1·02	1·19	0·46
1-Naphthylmethyl	1·51	1·66	1·05[b]
4-Methoxybenzyl	1·49	1·62	1·04[b]
2,4,6-Trimethylbenzyl	1·68	1·73	1·24[b]

[a] Measured in acetonitrile containing tetra-n-butylammonium perchlorate (0·1 M), substrate (10^{-3} M). Stationary Pt disc anode, voltage sweep rate 4 v/min.

[b] Onset of oxidation *ca.* 0·5 v.

A series of arylacetates has been studied voltammetrically and the results are shown in Table 1. These carboxylates all gave very broad oxidation peaks, except the caesium salt of 9-methylanthracene-10-acetic acid (I), the voltammogram of which is shown in the Figure. The semi-reversible couple

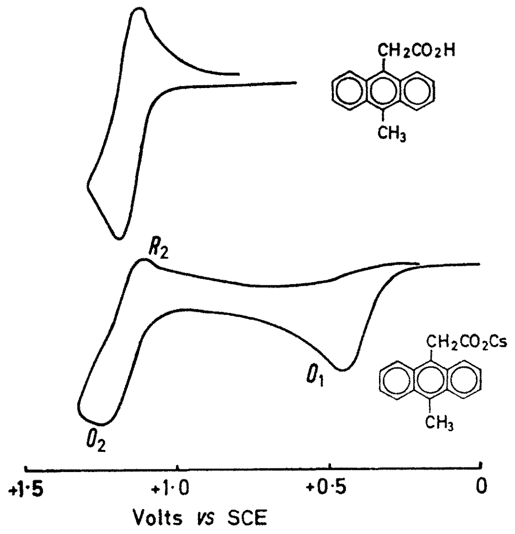


FIGURE. *Voltammograms in acetonitrile* (*as Table* 1).

O_2–R_2 appears to be due to the acid, formed from protons liberated at the first peak, O_1. That this acid is not formed in the solution prior to electrolysis can be shown by experiments with added pyridine. The possibility that O_2–R_2 is due to the α-nitrilium salt,[3] (IIIb), cannot be ruled out since the corresponding pyridinium derivative (IIIc) shows a completely reversible oxidation peak at 1·34 v, moving to less anodic values in the presence of nucleophiles. Preparative-scale oxidation of (I) [tetrahydrofuran/5M-methanol, +0·7 v *versus* SCE] gave a mixture of the dimer (II) [30%, based on (I) consumed] and the methyl ether (IIIa) [40%, based on (I) consumed].

It is probable that, of the carboxylates studied, only (I) gives the *pseudo*-Kolbe reaction. If (I) were oxidised *via* the carboxylate group, with concerted loss of CO_2, it would be expected that triphenylacetate ion, leading to a more stable benzylic radical and cation, would be oxidised even more easily. This is not the case, caesium triphenylacetate being oxidised at +1·00 v. Triphenylmethane is relatively difficult to oxidise (E_p = 1·96 v) so that triphenylacetate ion is unlikely to undergo the *pseudo*-Kolbe reaction. This indicates that electron transfer from the carboxylate, with assistance from the aryl group, possibly *via* a concerted reaction, is occurring with the carboxylates other than (I). This effect is demonstrated by successive phenyl substitution of acetic acid, as shown in Table 2.

TABLE 2

Voltammetry of phenyl-substituted acetate ions, $RCO_2^-Cs^+$

R	E_p (v *versus* SCE)[a,b]
CH_3	1·54
$PhCH_2$	1·43
Ph_2CH	1·27
Ph_3C	1·02

[a,b] As Table 1.

Contrary to previous findings with aliphatic acids,[4] the above results show that large differences can be observed in carboxylate oxidations on changing the substituents. These results are of relevance to the discussion of a concerted mechanism in the Kolbe reaction. However, under the voltammetric conditions employed, using a large excess of perchlorate, two-electron oxidation almost certainly occurs.[1]

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