

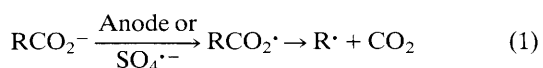
One-electron Oxidation of Carboxylates by Hexachloroosmate(v) Ion

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Hexachloroosmate(v) cleanly oxidizes tetrabutylammonium *tert*-butylcyanoacetate to decarboxylative-coupling products, *meso*- and *rac*-2,3-di-*tert*-butylsuccinonitrile, thus constituting the first metal ion-based oxidant to be found to simulate properly this aspect of the Kolbe anodic oxidation of carboxylates.

Hexachloroosmate(v), OsCl_6^- , is a strong one-electron oxidant¹ which reacts with neutral organic molecules in what seem to be clearcut outer-sphere electron transfer (ET) steps.² Since carboxylates, RCO_2^- , exhibit characteristic behaviour upon one-electron oxidation [eqn. (1)], for example in the Kolbe anodic synthesis³ or reaction with sulfate radical



($\text{SO}_4^{\cdot-}$),⁴ a further, stringent test of the hexachloroosmate oxidation mechanism was possible. The formation of dimers [eqn. (2)] demonstrates unequivocally the one-electron nature of the initial step, provided that further oxidation of the radical [eqn. (3)] can be avoided.

Carboxylates with electron-withdrawing groups, such as cyano or ethoxycarbonyl, in the α -position are known to produce oxidation-resistant radicals in eqn. (1). The second oxidation step, eqn. (3), is then disfavoured because of the destabilization of the carbocation,⁵ and only a minor part of the reaction proceeds along this pathway, *e.g.* in the Kolbe oxidation of α -carboxamido,⁶ -cyano⁷ and -ethoxycarbonyl⁸ substituted carboxylates.

Tetraphenylphosphonium hexachloroosmate(v) reacted with tetrabutylammonium *tert*-butylcyanoacetate or hydrogenbis(*tert*-butylcyanoacetate) $[\text{Bu}^t\text{CH}(\text{CN})\text{CO}_2]_2\text{H}^-$ in

dichloromethane or acetonitrile with the formation of coupling products in high yield [eqn. (4)]. In contrast to Kolbe⁷ or $\text{SO}_4^{\cdot-}$ oxidation,^{4a} the C-N coupling product [shown as the

Table 1 Products from the reaction between tetrabutylammonium hydrogenbis(*tert*-butylcyanoacetate) and tetraphenylphosphonium hexachloroosmate(v) in dichloromethane at ambient temperature

		Products (%)	
$[\text{H}(\text{RCO}_2)_2^-]/$ mol dm^{-3}	$[\text{OsCl}_6^-]/$ mmol dm^{-3}	NCCH(Bu ^t)- CH(Bu ^t)CN (<i>meso</i> : <i>rac</i>)	Bu ^t CH ₂ - CONHCH(CN)- Bu ^t
In MeCN			
0.10	20	1 : 2	0.1
1.0	100	26 : 17	—
1.0 ^a	100	30 : 20	—
1.0 ^b	90	12 : 3	—
In CH ₂ Cl ₂			
1.2	240	34 : 15	—
2.0	400	46 : 22	0.3
2.0	200	36 : 20	1
1.0	90	30 : 13	—
1.0 ^b	90	37 : 12	—
1.0 ^c	100	13 : 6	—

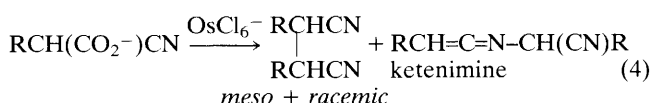
^a Water (10 vol %) added. ^b Water (0.5 vol %) added. ^c The neutral carboxylate salt was used.

Table 2 Acyloxy radical adducts from the oxidation of carboxylates and PBN by tetraphenylphosphonium hexachloroosmate(v) in dichloromethane

Carboxylate	[RCO ₂]/mol dm ⁻³	[PBN]/mol dm ⁻³	a ^N /mT	a ^H /mT	Adduct from
(AcO) ₂ H ⁻ after 18 h	1.03	0.22	1.36 1.46	0.16 0.22	CH ₃ CO ₂ Not established, but possibly HOCOCH ₂
(AcO) ₂ H ^{-a}	0.50	0.20	1.36	0.17	CH ₃ CO ₂
(AcO) ₂ H ⁻	0.29	0.20	1.36	0.16	CH ₃ CO ₂
Bu ^c CH(CN)CO ₂ ⁻	0.063	0.27	1.34	0.14	Bu ^c CH(CN)CO ₂ ^b
(Bu ^c CO ₂) ₂ H ⁻	0.038	0.29	1.36	0.14	Bu ^c CO ₂
PhCO ₂ ⁻	0.067	0.30	1.35	0.15	PhCO ₂ ^b
CF ₃ CO ₂ ⁻	0.18	0.19	1.33	0.14	CF ₃ CO ₂ ^b

^a HOAc (10 vol %) added. ^b This signal was weak, the predominant one being that of PhCON(O⁺)Bu^c (a^N = 0.81 mT), and disappeared within 20 min.

ketenimine in eqn. (4), but analysed as the corresponding amide after water treatment] was formed in small amounts only, even with water or methanol added to capture the



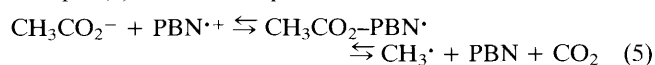
ketenimine before its possible conversion into the C–C coupling product. No evidence for the formation of any carbonium ion derived products was found, as expected from the high ionization energies of α-cyanoalkyl radicals (CNCH₂[•], 10.87 eV) and E⁰(OsCl₆⁻/OsCl₆²⁻) = 1.44 V vs. normal hydrogen electrode (NHE).² Only under conditions of Kolbe electrolysis, at anode potentials ≥2.3 V, might this process occur.

In contrast, tetrabutylammonium phenylacetate, which would produce the easily oxidizable benzyl radical [E⁰(PhCH₂[•]/PhCH₂⁺) = 0.97 V⁹], gave no coupling product but instead yielded the carbonium ion-derived product, benzyl phenylacetate in 60% yield.

Spin trapping experiments, in which the hexachloroosmate salt was allowed to react with a solution of the appropriate carboxylate (RCO₂⁻) and the spin trap, *N*-tert-butyl-α-phenylnitron (PBN, *N*-benzylidene-*tert*-butylamine *N*-oxide), did not give any evidence for the formation of spin adducts derived from R[•]. Instead, acyloxy spin adducts were formed (Table 2). Thus, hydrogendiacetate or acetate ion gave a spin adduct with a^N = 1.36 mT and a^H = 0.16 mT, in good agreement with literature values of 1.34 and 0.14 mT, respectively.¹⁰

In view of the extreme instability of the acetoxy radical and acyloxy radicals in general,¹¹ the acyloxy spin adduct is probably formed by oxidation of PBN (shown by cyclic voltammetry to be irreversibly oxidized at about 1.7 V) to its radical cation which then reacts with acetate to give the spin adduct.¹² Thus, the formation of an acyloxy spin adduct has no direct bearing on the hexachloroosmate(v)/RCO₂⁻ oxidation mechanism, but is relevant to the mechanism of spin adduct formation in redox systems. This was substantiated by choosing tris(4-bromophenyl)ammoniumyl ion as the oxidant; this species only reacts with bond formation with acetate and the extent of 'Kolbe-like' reaction was less than 0.001%.¹³ A spin trapping experiment with this oxidant produced the same acetoxy spin adduct as above, which must therefore originate from the radical cation of PBN.¹⁴

The acetoxy spin adduct was unstable, perhaps as a consequence of the inner-sphere electron-transfer mechanism of eqn. (5), and decomposed within hours (*k* = 0.03–0.06



min⁻¹ at 24 ± 1 °C), leaving behind a weak spin adduct signal, characterized by a^N = 1.46 mT and a^H = 0.22 mT. Under the

same conditions, the methyl radical PBN adduct [generated by MeLi treatment of PBN in benzene,¹⁵ followed by air oxidation and 100 times dilution with a medium consisting of dichloromethane and 0.8 mol dm⁻³ Bu₄N(AcO)₂H] had a^N = 1.52 and 0.334 mT and thus cannot be the origin of this signal. Possibly, the unknown signal might originate from the HOCOCH₂ spin adduct.

Thus, hexachloroosmate(v), like sulfate radical anion, is a reagent in homogeneous medium which will simulate the outcome of the Kolbe anodic oxidation of carboxylate. To the best of our knowledge, it is so far the only metal ion-based oxidant to possess this type of reactivity.

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References

- K. Dehnicke and R. Lössberg, *Z. Naturforsch., Teil B*, 1980, **35**, 1525; W. Preetz and M. Bruns, *Z. Naturforsch., Teil B*, 1983, **38**, 680; R. H. Magnuson, *Inorg. Chem.*, 1984, **23**, 387.
- L. Ebersson and M. Nilsson, *Acta Chem. Scand.*, 1990, **44**, 1062.
- L. Ebersson and J. H. P. Utley, in *Organic Electrochemistry*, ed. M. M. Baizer and H. Lund, 2nd edn., Dekker, 1982, ch. 14.
- (a) L. Ebersson, S. Gränse and B. Olofsson, *Acta Chem. Scand.*, 1968, **22**, 2462; (b) L. Ebersson, in ref. 3, ch. 28; (c) F. Minisci, A. Citterio and C. Giordano, *Acc. Chem. Res.*, 1982, **16**, 27.
- X. Creary, *Chem. Rev.*, 1991, **91**, 1625.
- L. Ebersson, *Acta Chem. Scand.*, 1963, **27**, 1196.
- L. Ebersson and S. Nilsson, *Acta Chem. Scand.*, 1968, **22**, 2453.
- L. Ebersson and B. Sandberg, *Acta Chem. Scand.*, 1966, **20**, 739.
- D. D. M. Wayner and D. Griller, *J. Am. Chem. Soc.*, 1985, **107**, 7764.
- W. A. Pryor, C. K. Govindan and D. F. Church, *J. Am. Chem. Soc.*, 1982, **104**, 7563.
- See, e.g. W. Braun, L. Rajbenbach and F. R. Eirich, *J. Phys. Chem.*, 1962, **66**, 1591; R. Kaptein, J. Brokken-Zijp and F. J. J. de Kanter, *J. Am. Chem. Soc.*, 1972, **94**, 6280; J. Chateaufort, J. Luszyk and K. U. Ingold, *J. Am. Chem. Soc.*, 1988, **110**, 2886; J. Chateaufort, J. Luszyk, B. Maillard and K. U. Ingold, *J. Am. Chem. Soc.*, 1988, **110**, 6727.
- E. G. Janzen and B. J. Blackburn, *J. Am. Chem. Soc.*, 1969, **91**, 4481; G. Gronchi, PhD Thesis, University of Aix-Marseille, 1984; G. Gronchi, P. Courbis, P. Tordo, G. Mousset and J. Simonet, *J. Phys. Chem.*, 1983, **87**, 1343; V. Cerri, C. Frejaville, F. Vila, A. Alouche, G. Gronchi and P. Tordo, *J. Org. Chem.*, 1989, **54**, 1447; I. M. Sosonkin, V. N. Belevskii, G. N. Strogov, A. N. Domarev and S. P. Yarkov, *J. Org. Chem. USSR (Engl. Transl.)*, 1982, **18**, 1504; H. Chandra and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 1986, 1301.
- L. Ebersson and B. Larsson, *Acta Chem. Scand., Ser. B*, 1986, **40**, 210; L. Ebersson and B. Olofsson, *Acta Chem. Scand.*, 1989, **43**, 698.
- L. Ebersson, *J. Chem. Soc., Perkin Trans. 2*, in the press.
- E. G. Janzen and B. J. Blackburn, *J. Am. Chem. Soc.*, 1968, **90**, 5910.