Electron Transfer Reactions in Organic Chemistry. XXIII.[†] Products, Kinetics and Inverted Spin Trapping in the Reaction between Carboxylates and Hexachloroosmate(V) Ion

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The reaction between carboxylates and hexachloroosmate(V) has been investigated. For carboxylates, RCOO$^-$, corresponding to radicals R· which are difficult to oxidize (with E_i larger than ~9 eV) the reaction gave one-electron oxidation products, as typified by the formation of C-to-N coupling products in good yield from tert-butylcyanoacetate ion. The kinetics of the reaction between the hydrogendiacetate ion and OsCl$_6^-$ in acetonitrile was studied in more detail and found to conform to a kinetic model involving a second-order electron-transfer step between acetate ion (existing in equilibrium with acetic acid and hydrogendiacetate ion) and OsCl$_6^-$.

Attempts to trap R· from the carboxylate/hexachloroosmate reaction by α-phenyl-N-tert-butylnitrone (PBN) led only to the formation of acyloxyl spin adducts, presumably via the reaction between PBN·$^+$ (formed by one-electron oxidation of PBN by the osmate) and the carboxylate ion. Other nucleophiles underwent the same type of reaction, previously denoted 'inverted spin trapping', and also the more oxidation-resistant spin trap 4-NO$_2$PBN was shown to possess this type of reactivity.

Hexachloroosmate(V), OsCl$_6^-$, is a strong one-electron oxidant toward organic molecules.[1–3] By comparison with established outer-sphere electron transfer (ET) reactions between tris(phenanthroline)iron(III) complexes[4] or 12-tungstocobaltate(III)[5] and neutral organic substrates, it has been shown[2,3] that hexachloroosmate(V) also approximates to outer-sphere behaviour in analogous processes with alkylmetals and aromatic compounds. Since carboxylates, RCOO$^-$, show a characteristic product pattern upon one-electron oxidation [eqns. (1) and (2)], as exemplified by the Kolbe anodic oxidation[6] or reaction with sulfate radical (SO$_4^{·-}$),[7] it was of interest

$$RCOO^- \xrightarrow{-e^-} RCOO· \rightarrow R· + CO_2 \tag{1}$$

$$2R· \longrightarrow R–R \tag{2}$$

$$R· \xrightarrow{-e^-} R^+ \tag{3}$$
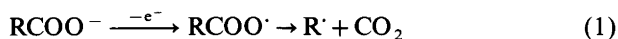
to test the hexachloroosmate(V) oxidation mechanism by reacting it with a series of carboxylates with different R groups. Dependent upon the nature of R, products can be

directed toward the formation of predominantly dimers R–R or carbocation-based products [eqn. (3)]. The formation of dimers according to eqn. (2) is unambiguous evidence that the initial step must be a one-electron oxidation.

If R is substituted with an electron-withdrawing group, for example a cyano or alkoxycarbonyl group, at the α carbon, the ET step of eqn. (3) becomes slow and thus formation of dimers is favored. Only a minor proportion of products is formed via the carbocation pathway, presumably because of the destabilization of R$^+$ by electron-withdrawing substituents.[8] Examples can be found in the sulfate radical or Kolbe oxidation of α-carboxamido,[9] -cyano[10] and -ethoxycarbonyl[11] substituted carboxylates. In a preliminary communication[12] we have shown that hexachloroosmate(V) cleanly oxidized tetrabutylammonium tert-butylcyanoacetate to decarboxylative-coupling products and we now report a more detailed study of this carboxylate as well as of other carboxylates.

Results of product studies

Reaction between OsCl$_6^-$ and tert-butylcyanoacetate *ion.* Tetraphenylphosphonium hexachloroosmate(V) reacted
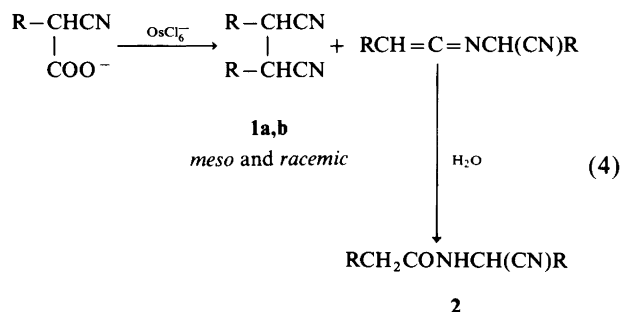
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† For part XXII, see Ref. 3.
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with tetrabutylammonium *tert*-butylcyanoacetate or hydrogendi(*tert*-butylcyanoacetate),
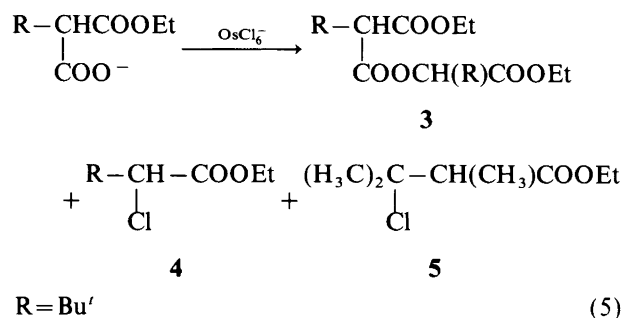
$$[\text{Bu}^t\text{CH(CN)COO}]_2\text{H}^-,$$

in dichloromethane or acetonitrile with the formation of coupling products **1** and **2** [eqn. (4), $R = \text{Bu}^t$] in high yield (see Table 1). A property of α-cyanoalkyl radicals is their two-site reactivity in coupling; both in Kolbe anodic and sulfate radical oxidation of α-cyanocarboxylates C-to-C (succinonitriles) and C-to-N (ketenimines, eventually transformed into amides **2** and analyzed as such) coupling is observed.[7,10] In contrast, hexachloroosmate(V) oxidation gave only small amounts of the C-to-N coupling product, maximally 1 % yield. No evidence for the formation of carbonium-ion-derived products, such as the rearrangement product 2,3-dimethyl-2-butenenitrile,[4] was found.

R−CHCN $\xrightarrow{\text{OsCl}_6^-}$ R−CHCN + RCH=C=NCH(CN)R
| |
COO⁻   R−CHCN

1a,b

meso and *racemic*   H₂O   (4)

$\text{RCH}_2\text{CONHCH(CN)R}$

2

Reaction between OsCl₆⁻ and tert-*butylethoxycarbonylacetate ion.* With a ratio of carboxylate : oxidant of 10 : 1 in dichloromethane, this reaction gave no coupling product, similarly to eqn. (2) but instead products (**3–5**) that presumably were formed via an intermediate car-

bocation. Analysis of the product mixture by GLC–MS indicated the presence of ester **3** in 3–5 % yield, a known product type in Kolbe couplings,[6] and two compounds **4** and **5** (total 40 %) containing one chlorine atom with $M^+ = 178$. In analogy with previously established behaviour of α-ethoxycarbonyl substituted carbocations,[11] we assign structures **4** and **5** to these products. In addition, the formal decarboxylation product of the starting material, ethyl 3,3-dimethylbutyrate (**6**), was detected in 10–20 % yield. When the RCOO⁻: oxidant ratio was 1 : 1, only **4 + 5** and **6** were found in 40 and 6 % yield,

R−CHCOOEt $\xrightarrow{\text{OsCl}_6^-}$ R−CHCOOEt
| |
COO⁻   COOCH(R)COOEt

3

      R−CH−COOEt   (H₃C)₂C−CH(CH₃)COOEt
+ | + |
       Cl   Cl

      4   **5**

$R = \text{Bu}^t$ (5)

respectively. Here a hint was obtained that chloride ion might be liberated from the oxidant and interfere in the chemical follow-up steps.

Reaction between OsCl₆⁻ and trifluoroacetate ion. This reaction (ratio carboxylate : oxidant = 7–10 in dichloromethane) invariably gave small and varying amounts of trifluoromethane and trifluorochloromethane (total yield 5–50 %), presumably mostly due to the difficulties involved in quantifying very small amounts of gaseous

Table 1. Products from the reaction between tetrabutylammonium hydrogendi(*tert*-butylcyanoacetate) and tetraphenylphosphonium hexachloroosmate(V) at ambient temperature.

| | | Products (% yield) | | |
| | | NCCH(Buᵗ)CH(Buᵗ)CN | | |
[H(RCOO)₂H⁻]/M	[OsCl₆⁻]/mM	*meso*	Racemic	BuᵗCH₂CONH–CH(CN)Buᵗ
In CH₃CN				
0.10	20	1	2	0.1
1.0	100	26	17	—
1.0ᵃ	100	30	20	—
1.0ᵇ	100	12	3	—
In CH₂Cl₂				
1.2	240	34	15	—
2.0	400	46	22	0.3
2.0	200	36	20	1
1.0	90	30	13	—
1.0ᵇ	90	37	12	—
1.0ᶜ	100	13	6	—

ᵃWater (10 vol %) added. ᵇWater (0.5 vol %) added. ᶜThe neutral carboxylate salt was used.

products. No hexafluoroethane, the predominant coupling product from Kolbe oxidation,[13] was detected.

Reaction between $OsCl_6^-$ and acetate ion. Again, technical difficulties in analyzing small amounts of gaseous products caused problems, so that it was only possible to establish that methyl chloride was the major gaseous product at a yield level of ~15% from a run with the carboxylate in large excess over oxidant, 25 : 1, with dichloromethane as the solvent. Methane, in ~0.02% yield, was also detected, but not ethane. No methyl acetate, a possible product of the carbocation pathway,[6] was detected.

Reaction between $OsCl_6^-$ and phenylacetate ion. The reaction between hexachloroosmate(V) and tetrabutyl-ammonium phenylacetate in dichloromethane gave no coupling product (bibenzyl) but instead gave the carboca-tion-derived product, benzyl phenylacetate in 60% yield.

Reaction between $OsCl_6^-$ and chloride ion. In view of the possibility that chloride ion might be liberated during reactions of $OsCl_6^-$ the reaction between an excess of tetrabutylammonium chloride and $OsCl_6^-$ in acetonitrile (ratio 6 : 1) was carried out. When the redox process was over, cyclohexene was added and the product mixture analyzed (GLC–MS) for 1,2-dichlorocyclohexane. This compound was positively identified in low yield (0.5%) showing that some chlorine was formed in the redox reaction.

Results of kinetic studies

Reaction between $OsCl_6^-$ and tetrabutylammonium chloride. This reaction was carried out in acetonitrile, the absorption maximum of the Os(V) species at 500 nm being monitored, and revealed a potential source of systematic error arising from the use of tetrabutylam-monium salts. Different batches of tetrabutylammonium chloride gave significantly different pseudo-first-order rate constants (with excess of [Cl^-]), and this behaviour was eventually found to depend on the presence of small and varying amounts of tributylamine in the salt. This impurity could be removed by washing the salt with dry diethyl ether; GLC analysis showed that the wash liquid contained tributylamine and that a second washing did not remove any more tributylamine from the salt. Fig. 1 shows the effect of using a sample of salt before and after washing in the low range of [Cl^-]. However, even with thoroughly washed samples, the kinetics showed erratic behavior and we therefore refrained from quantitative evaluation. Presumably the relatively high basicity of chloride ion in acetonitrile[14] promotes an elimination reaction in the stock solution of the salt. In itself, tributylamine reacted immeasurably fast with $OsCl_6^-$ at a concentration level of ~1 mM using the kinetics equipment available to us, meaning that the second-order rate constant must be $\geqslant (1-2) \times 10^6 \ M^{-1} s^{-1}$.
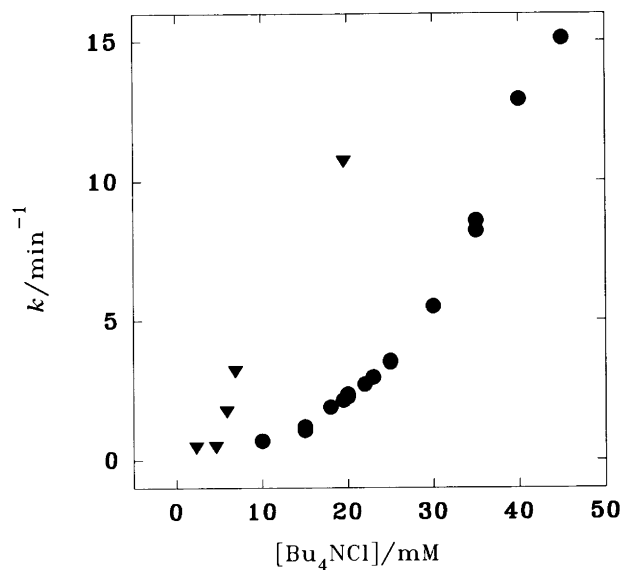

Fig. 1. Observed rate constants, k, for the reaction between $OsCl_6^-$ and tetrabutylammonium chloride as a function of [Bu_4NCl]: $\triangledown$, untreated Bu_4NCl; ●, same Bu_4NCl sample, washed with diethyl ether.

Reaction between $OsCl_6^-$ and very weak nucleophiles. Tetrabutylammonium perchlorate or trifluoromethane-sulfonate did not undergo any redox reaction with $OsCl_6^-$ in acetonitrile. Here we are dealing with very weakly nucleophilic/basic anions of high resistance toward ET oxidation. No elimination to give tributylamine was expected. Also weak neutral nucleophiles of high resistance toward ET oxidation, such as water, methanol and acetonitrile, did not undergo any redox reaction with $OsCl_6^-$.

Reaction between $OsCl_6^-$ and carboxylates. With the above results as background, it could be ascertained that the redox reaction between tetrabutylammonium hydrogendicarboxylates [$Bu_4N(RCOO)_2H$, used because of their convenient handling as compared with the very hygroscopic nature and purification difficulties of car-boxylate salts] and $OsCl_6^-$ was not due to any tributylamine present in the salt (see the Experimental).

Tetrabutylammonium hydrogendi(*tert*-butylcyano-acetate) (4.1 mM) reacted with $OsCl_6^-$ (0.15 mM) in acetonitrile in a redox process which was zero-order in Os(V), its rate of disappearance being ~7 AU (absorbance units) s^{-1}.

Since the hydrogendiacetate ion exists in equilibrium with acetic acid and acetate ion [eqn. (6), $K_{diss} = 2.1 \times 10^{-4} \ M$ (Ref. 15)], we first tested the possibility that only acetate ion would be the kinetically active species by adding acetic acid in increasing concentration. As seen from Fig. 2, acetic acid slowed down the reaction to essentially zero rate at relatively high [HOAc] (1.7 M).[1,2] On the assumption that acetate ion is the kinetically
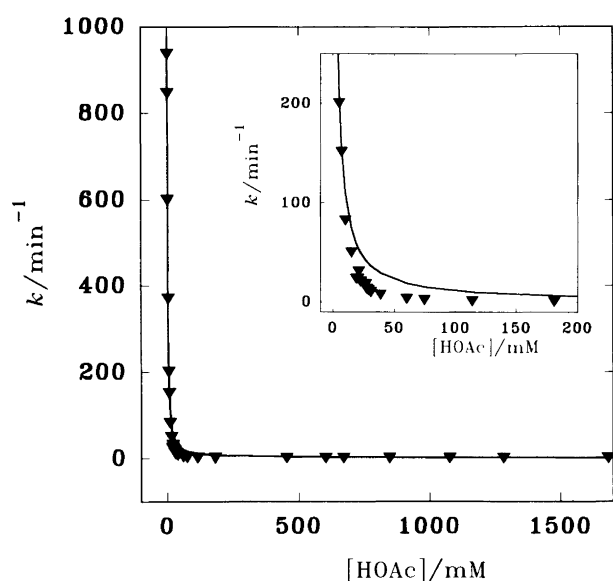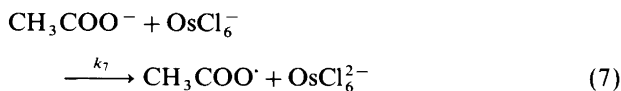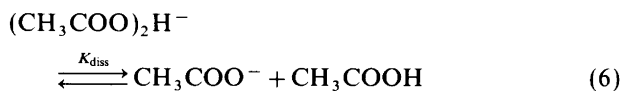
Fig. 2. Observed rate constants, k, for the reaction between $OsCl_6^-$ and tetrabutylammonium hydrogendiacetate (4.8 mM in all runs) as a function of added [HOAc]. The solid curve represents the best fit of the analytical expression for the mechanism of eqns. (6) and (7), giving $K_{diss} = 2.3(3) \times 10^{-4}$ M and $k_7 = 1.7(1) \times 10^4$ M^{-1} s^{-1}. The insert shows an enlarged portion of the plot.

active species in a straight-forward second-order reaction with hexachloroosmate(V) [eqn. (7)], the data were

$$(CH_3COO)_2H^-$$

$$\xrightleftharpoons{K_{diss}} CH_3COO^- + CH_3COOH \qquad (6)$$

$$CH_3COO^- + OsCl_6^-$$

$$\xrightarrow{k_7} CH_3COO^{\cdot} + OsCl_6^{2-} \qquad (7)$$

fitted to the corresponding kinetic expression,[16] giving $k_7 = 1.7(1) \times 10^4$ M^{-1} s^{-1} and $K_{diss} = 2.3(3) \times 10^{-4}$ M,

the latter quantity being in excellent agreement with the literature value[15] (see above).

Tetrabutylammonium hydrogendiacetate itself reacted with $OsCl_6^-$ in acetonitrile in a redox process which exhibited pseudo-first-order behavior at any given concentration of $[(AcO)_2H^-]$ in the range 1.4–30 mM. Using the above value of K_{diss}, as evaluated from the data of Fig. 2, $[AcO^-]$ was calculated for each $[(AcO)_2H^-]$ and used to compute $k_7 = 1.8(5) \times 10^4$ M^{-1} s^{-1}, in good agreement with that obtained from runs in the presence of added HOAc (Fig. 2).

Runs with tetrabutylammonium acetate (washed with diethyl ether) in the concentration range 2–10 mM gave a series of pseudo-first-order rate constants from which k_7 came out approximately twice as large, $3.8(5) \times 10^4$ M^{-1} s^{-1}. This might be due to small amounts of tributylamine left in the salt and/or formed in the stock solution by the elimination reaction.

Reaction between $OsCl_6^-$ and trinitromethanide ion. The reaction between $OsCl_6^-$ (0.15 mM) and tetrabutylammonium trinitromethanide (3.9 mM), a relatively weak nucleophile in acetonitrile,[17] was a redox process which was zeroth order in $[OsCl_6^-]$, the rate of its disappearance being 5×10^{-3} AU min^{-1}.

Results of spin trapping experiments

The preparative results described above clearly showed that the $OsCl_6^-$ oxidation of *tert*-butylcyanoacetate ion takes place via the radical intermediate $R^{\cdot}$ of eqn. (1), since dimers were formed in good yield [eqn. (4)]. There were also indications that radicals were intermediates in the oxidation of acetate or trifluoroacetate ion (see the Discussion), and attempts were therefore made to apply the technique of spin trapping and identification of the intermediate radical by the characteristics of the EPR spectrum of the spin adduct.[18]

We used *N-tert*-butyl-α-phenylnitrone (PBN; IUPAC name: *N*-benzylidene-*tert*-butylamine *N*-oxide) as the

Table 2. Acyloxyl radical adducts from the oxidation of carboxylates (as tetrabutylammonium salts) and PBN by tetraphenylphosphonium hexachloroosmate(V) in dichloromethane at ~20°C.

Carboxylate	[RCOO⁻]/ mol dm⁻³	[PBN]/ mol dm⁻³	a^N/mT	a^H/mT	Spin adduct from
$(AcO)_2H^-$	1.03	0.22	1.36	0.16	CH_3COO
after 18 h			1.46	0.22	Possibly $HOCOCH_2$ (see text)
$(AcO)_2H^{-a}$	0.50	0.20	1.36	0.17	CH_3COO
$(AcO)_2H^-$	0.29	0.20	1.36	0.16	CH_3COO
AcO^-	0.64	0.25	1.33	0.14	CH_3COO^b
AcOH alone	0.60	0.20	1.36	0.17	CH_3COO^c
$Bu^tCH(CN)COO^-$	0.063	0.27	1.34	0.14	$Bu^tCH(CN)COO^d$
$(Bu^tCOO)_2H^-$	0.038	0.29	1.36	0.14	Bu^tCOO
$PhCOO^-$	0.18	0.30	1.35	0.15	$PhCOO^d$
CF_3COO^-	0.18	0.19	1.33	0.14	CF_3COO^d

[a]HOAc (10 vol %) added. [b]The spectrum of this spin adduct was eventually replaced by the 3×0.81 mT spectrum of $PhCON(O^{\cdot})Bu^t$ (X). [c]Formed together with a strong signal from X. [d]Weak signal, accompanied by a strong signal from X.

Table 3. Spin adducts from the oxidation of solutions of nucleophiles, Nu^- (anionic ones as tetrabutylammonium salts), and PBN by tetraphenylphosphonium hexachloroosmate(V) in dichloromethane at 20°C.

Nucleophile, Nu^-	$[Nu^-]/$ mol dm^{-3}	$[PBN]/$ mol dm^{-3}	a^N/mT	a^H/mT	Spin adduct from
$(NO_2)_3C^-$	0.068	0.026	1.47	0.45	$(NO_2)_3C$
Tetramethylsuccinimide anion	0.13	0.25	1.43	0.52	N-Tetramethylsuccinimidyl ($a^{N'} = 0.133$)
Tetramethylsuccinimide as such	0.20	0.25	0.81	—	$O=$
1,2,3-1H-Triazole as such	0.21	0.16	1.41	0.17	N1-1,2,3-Triazolyl ($a^{N'} = 0.337$ mT)
Benzotriazole anion	0.073	0.16	1.38	0.16	N1-Benzotriazolyl ($a^{N'} = 0.352$ mT)
Benzotriazole as such	0.13	0.17	1.38	0.16	N1-Benzotriazolyl ($a^{N'} = 0.352$ mT)
1H-Tetrazole as such	0.20	0.16	1.41	0.17	N1-Tetrazolyl ($a^{N'} = 0.306$ mT)
3,5-Lutidine	0.11	0.17			No spin adduct seen
CN^-	0.064	0.20			No spin adduct seen
$(EtO)_3P$	0.069	0.18	1.47	0.347	$(EtO)_3P^+$ ($a^P = 2.34$ mT)

spin trap, expecting that the spin adduct of $R^·$ of eqn. (1) would be detectable, as shown in eqn. (8). However, the

$$PhCH = N(O)Bu^t + R^· \rightarrow PhCH(R)-N(O^·)Bu^t \qquad (8)$$

spin adducts formed turned out to be of acyloxyl type, i.e., the trapped radical was seemingly RCOO$^·$ (Table 2). Acyloxyl spin adducts have quite different hfs values from alkyl spin adducts,[18] and a careful search for R–PBN$^·$ from the oxidation of acetate or trifluoroacetate ($R = CH_3$ or CF_3) did not show any trace of R–PBN$^·$, even when the reactions were monitored over long reaction times (24–48 h). Under the same conditions $CH_3PBN^·$ had $a^N = 1.52$ and $a^H = 0.334$ mT and $CF_3PBN^·$ $a^N = 1.42$, $a^H = 0.188$ and $a^F = 0.147$ mT, the further splitting by the fluorine atoms being a characteristic and easily recognizable feature of the latter radical.

The acyloxyl adducts were unstable and decayed rather rapidly. The disappearance of the acetoxyl adduct was monitored at $24 \pm 1°C$ and found to occur with a rate constant of $0.03–0.06$ min^{-1}. A weak spin adduct signal was left behind, $a^N = 1.46$ and $a^H = 0.22$ mT, possibly due to $HOCOCH_2PBN^·$ formed by decomposition of the acetoxyl adduct. Attempts to generate this radical by photolysis of chloro- or bromo-acetic acid under conditions as closely as possible simulating those of the $OsCl_6^-$ experiments,[19] were not decisive. Several spin adducts were formed in low concentrations, but it was not possible to establish their origin with certainty (see the Experimental).

Since acyloxyl radicals are highly unstable toward decarboxylation (typically, rate constants fall in the interval $10^7–10^9$ s^{-1} (Ref. 20), it was unlikely that they were trapped as such; instead, a mechanism involving initial one-electron oxidation of PBN to its radical cation, $PBN^{·+}$, followed by reaction of the latter with the nucleophilic carboxylate to give the formal spin adduct, $PBN–OCOR^·$, was implicated. This idea could be better tested by using tris(4-bromophenyl)aminium radical cation as the oxidant, since it was known that a number of nucleophiles do not undergo ET with this reagent. It was found that a wide variety of nucleophiles gave PBN spin adducts in this way.[21]

Thus the detection of acyloxyl spin adducts from the $OsCl_6^-/RCOO^-/PBN$ reaction is, in all likelihood, not relevant for the mechanism of the reaction between $OsCl_6^-$ and $RCOO^-$. However, the possible incursion of radical cations of spin traps in attempts to detect radicals from redox reactions is of great principal interest, since it represents a difficult interpretational problem. The behavior of hexachloroosmate(V), a high-potential one-electron oxidant capable of oxidizing organic compounds in outer-sphere processes, in this type of reaction (denoted 'inverted spin trapping' = IST) is therefore of importance for delineating the scope of inverted spin trapping. We therefore extended the list of nucleophiles beyond carboxylates, as shown in Table 3. Indeed spin adducts were also formed from other nucleophiles in much the same way as when tris(4-bromophenyl)-aminium was used as the oxidant,[21] although some

Table 4. Spin adducts from the oxidation of solutions of nucleophiles, Nu^- (anionic ones as tetrabutylammonium salts), and 4-NO_2-PBN by tetraphenylphosphonium hexachloroosmate(V) in dichloromethane at 20°C.

Nucleophile, Nu^-	$[Nu^-]/$ mol dm^{-3}	$[NO_2\text{-}PBN]/$ mol dm^{-3}	a^N/mT	a^H/mT	Spin adduct of
$(NO_2)_3C^-$	0.018	0.12	1.45	0.368	$(NO_2)_3C^a$
AcO^-	0.10	0.15	0.77	—	$O=$
$(AcO)_2H^-$	0.055	0.19	0.77	—	$O=$
Benzotriazole anion	0.099	0.19	1.46	0.31	3 × 2; no sign of 3 × 3 × 2 signal
Benzotriazole as such	0.14	0.13	1.41	0.15	N1-Benzotriazolyl ($a^{N'} = 0.338$ mT)
$(EtO)_3P$	0.069	0.18	1.47	0.324	$(EtO)_3P^+$ ($a^P = 2.40$ mT)

^{a}Triplet (3 × 0.77 mT), in all probability due to 4-NO_2-$C_6H_4CON(O^·)Bu^t$.

exceptions were noted (3,5-lutidine, cyanide ion). 1,2,3-1H-Triazole and derivatives thereof turned out to be very effective in giving spin adducts by IST, even when used in unionized form.[22]

The use of a spin trap of higher redox potential, 4-NO_2PBN, oxidized at a potential about 0.4 V more positive than that of PBN (see the Experimental), is demonstrated in Table 4. Three nucleophiles, trinitromethanide ion, benzotriazole and triethyl phosphite, still gave spin adducts derived from this trap; the carboxylates gave what presumably must be the acyl nitroxide [4-$NO_2C_6H_4$CON(O·)Bu', characterized by a 3×0.77 mT triplet; cf. the acyl nitroxide of PBN itself with a 3×0.80 mT triplet)].

Discussion

The radical nature of the reaction between carboxylates and $OsCl_6^-$. Unambiguous evidence for the intervention of radicals, R· [eqn. (1)], was obtained only in the case of *tert*-butylcyanoacetate where dimers resulting from both C-to-C coupling and C-to-N coupling of α-cyanoalkyl radicals were formed in good yield (Table 1). This must be due to the high ionization potential (E_i^{23}) of this type of radical (E_i of $NCCH_2^· = 10.9$ eV and of $NC(CH_3)_2C^· = 9.2$ eV, placing E_i of a monoalkylated cyanomethyl radical at ~ 10 eV) which makes it unreactive toward further oxidation by $OsCl_6^-$ [eqn. (3)]. On the other hand, phenylacetate, giving rise to the benzyl radical ($E_i = 7.6$ eV) upon one-electron oxidation, gave no indication of radical-based products such as bibenzyl. Even α-ethoxycarbonyl radicals [eqn. 5)] (for which E_i values do not appear to have been measured) which upon both Kolbe and sulfate radical anion oxidation gave predominantly dimers,[4,11] did not give this type of product in the presence of $OsCl_6^-$.

For trifluoroacetate, the corresponding radical of which has $E_i = 9.2$ eV, the situation is also clear cut, insofar as CF_3H was detected among the products. This compound can hardly be formed in any way other than by H atom abstraction from the solvent by $CF_3^·$, a radical difficult to oxidize. The second product, chlorotrifluoromethane, cannot unambiguously be ascribed to $CF_3^·$ abstracting a chlorine atom from a chloro complex, although the alternative pathway, formation of CF_3^+ appears less likely in view of the high ionization potential of $CF_3^·$. Finally, the acetate ion results indicate methyl radical intervention, since methyl radical is rather difficult to oxidize ($E_i = 9.8$ eV) and thus might be the origin of the methyl chloride formed.

One conclusion from the above results is that only radicals which are difficult to oxidize will survive further oxidation by hexachloroosmate(V). The borderline for resistance toward further ET oxidation can be put at ~ 9 eV.

The kinetic studies of the reaction between tetrabutylammonium chloride and $OsCl_6^-$ were com-

plicated by the high reactivity of tributylamine, present as an impurity in all samples tried by us. The amine could be washed away by dry diethyl ether but even so a quantitative evaluation of the kinetics could not be reliably performed because of the possibility of an elimination reaction in the stock solution. The very fast reaction between tributylamine and $OsCl_6^-$ is expected in view of the exergonicity of the ET step, $E_{pa}(Bu_3N^{·+}/Bu_3N)$ being of the order of 1.0 V.[24] Difficulties due to this elimination process are to be expected with tetrabutylammonium salts of other strong bases, such as fluoride ion (and indeed we could not get tetrabutylammonium fluoride samples pure enough for studies involving $OsCl_6^-$ as the oxidant).

The reaction between $OsCl_6^-$ and tetrabutylammonium hydrogendiacetate in acetonitrile was slowed down and eventually almost completely arrested by added HOAc, indicating that the stronger nucleophile, acetate ion, is the kinetically active species of the rapid equilibrium of eqn. (6). With the additional assumption that the ET reaction between acetate ion and $OsCl_6^-$ is a straightforward second-order step (rate constant k_7), an analytical expression for the pseudo-first-order rate constant, k, of Fig. 2 as a function of [HOAc] was derived, using K_{diss} and k_7 as disposable parameters. The best fit of this equation to the data of Fig. 2 gave $K_{diss} = 2.3(3) \times 10^{-4}$ M and $k_7 = 1.7(1) \times 10^4$ M^{-1} s^{-1}. The literature value[15] of K_{diss} is 2.1×10^{-4} M, in very good agreement with the value above, considering the possible imperfections of the model.

The rate constant k_7 can be calculated by the Marcus treatment, assuming that the reaction is of the outer-sphere type. Such calculations are commented upon below in another context; here it suffices to note that values of $E^°(CH_3COO^·/CH_3COO^-) = 1.9$ V and 1.6 V in acetonitrile give theoretical k_7 values of 6×10^2 and 6×10^{-5} M^{-1} s^{-1}, respectively, again a satisfactory agreement in view of the uncertainty of the acetoxyl/ acetate potential. The choice of two values of this parameter is dictated by the occurrence of two estimates in the literature,[25,26] 2.4 and 2.1 V, respectively. The correction for moving acetate ion from water to acetonitrile was taken to be 0.5 eV.[27]

Attempts to trap radicals R· formed according to eqn. (1), using acetate and trifluoroacetate, by the spin trap PBN [eqn. 7)] failed. Instead the acyloxy radical adducts were detected, pointing to the predominance of another mechanism[21] of spin trapping, namely initial oxidation of the spin trap to its radical cation, which then reacts with a nucleophile present [eqn. (9), Nu$^-$ = RCOO$^-$] to give a spin adduct indistinguishable from

$$PBN + OsCl_6^- \longrightarrow PBN^{·+} + OsCl_6^{2-}$$

$$\Big\downarrow Nu^- \qquad\qquad (9)$$

$$PBN–Nu^·$$

that formed via eqn. (8). Strong support for this type

Table 5. Calculated rate constants of outer-sphere ET reactions of different charge types for three representative substrate standard potentials. $E°(Os^V/Os^{IV})$ was taken to be 1.40 V and r_{12} to be 6.1 Å.

Substrate type	$E°/V$	$\Delta G°/$ kcal mol^{-1}	Electrostatic corr./ kcal mol^{-1} *a*	$\Delta G°'/$ kcal mol^{-1} *b*	$\Delta G_a^{\ddagger}/$ kcal mol^{-1} *c*	$\Delta G_c^{\ddagger}/$ kcal mol^{-1} *d*	$\Delta G^{\ddagger}/$ kcal mol^{-1} *e*	log k_{ET} *f*
In CH$_2$Cl$_2$ ($D = 8.9$)								
A	1.7	6.9	−12.2	−5.3	3.9	0	3.9	8.1
A$^-$	1.7	6.9	−6.1	0.8	6.7	6.1	12.8	1.6
A	2.1	16.1	−12.2	3.9	8.3	0	8.3	5.1
A$^-$	2.1	16.1	−6.1	10.0	12.2	6.1	18.3	−2.5
A	2.4	23.1	−12.2	10.9	12.9	0	12.9	1.5
A$^-$	2.4	23.1	−6.1	17.0	17.6	6.1	23.7	−6.4
In CH$_3$CN ($D = 36.2$)								
A	1.7	6.9	−3.0	3.9	8.4	0	8.4	4.8
A$^-$	1.7	6.9	−1.5	5.4	9.2	1.5	10.7	3.1
A	2.1	16.1	−3.0	13.1	14.5	0	14.5	0.3
A$^-$	2.1	16.1	−1.5	14.6	15.7	1.5	17.2	−1.6
A	2.4	23.1	−3.0	20.1	20.3	0	20.3	−3.9
A$^-$	2.4	23.1	−1.5	21.6	21.7	1.5	213.2	−6.1

a Equal to $[(Z_1 - Z_2 - 1) \ 331.2]/(r_{12}D)$, where Z_1 and Z_2 are the charges of the oxidant and reductant, respectively, D is the relative permittivity and r_{12} is the distance between the spherical reactants in the collision complex. *b* Equal to $\Delta G° +$ the electrostatic term of note *a*. *c* The free energy of activation, as calculated by the Marcus quadratic expression, $[\lambda(1 + \Delta G°'/\lambda)^2]/4$. *d* The electrostatic contribution to the free energy of activation $= (331.2 Z_1 Z_2)/(r_{12}D)$. *e* Equal to $\Delta G_a^{\ddagger} + \Delta G_c^{\ddagger}$. *f* Equal to $11 - \Delta G^{\ddagger}/(2.303 RT)$.

of mechanism has been provided elsewhere for a range of nucleophiles (including fluoride ion), using tris-(4-bromophenyl)aminium ion as the oxidant.[21] The mechanism has been denoted 'inverted spin trapping'; it is of little relevance for mechanistic studies of putative radical reactions but is of utmost importance for the correct assessment of mechanisms of reactions involving thermal and/or photochemical redox processes when the spin trapping technique is applied.

For OsCl$_6^-$ induced spin trapping, a few model reactions were analyzed by the Marcus treatment (Table 5).[28] The substrates were of neutral and negatively charged type (A and A$^-$) and calculations for substrate potentials of 1.7, 2.1 and 2.4 V were performed, using a λ value ($\lambda =$ the reorganization energy) of 25 kcal mol^{-1} for all reactions. The two lower substrate potentials were chosen to correspond approximately to the peak potentials of the PBN$^{\cdot +}$/PBN and 4-NO$_2$PBN couples. The most significant result of these calculations is the very strong influence of the electrostatic corrections in a low relative permittivity solvent like dichloromethane; the reaction between OsCl$_6^-$ and the neutral substrate (corresponding to the spin trap) is 10^6–10^8 times faster than with the negatively charged one (corresponding to, e.g., RCOO$^-$) in the potential interval examined. In acetonitrile, the same trend is obtained although it is weaker, $\sim 10^2$. Thus the competition between the reactions between OsCl$_6^-$ and PBN or a negatively charged nucleophile is overwhelmingly in favor of the former, especially in low relative permittivity solvents of the type commonly used in spin trapping (benzene, toluene, dichloromethane). The formation of spin adducts from other negatively

charged nucleophiles in the OsCl$_6^-$/PBN system is amply demonstrated by the data of Table 3. On the other hand, if the competition for the oxidant is between two neutral compounds (or, generally, two compounds of the same charge type), the selectivity will largely be determined by the oxidation potentials of the substrates. Thus if for example tributylamine is present even as an impurity (as shown above) in a tetrabutylammonium salt (e.g., chloride, fluoride or cyanide which did not give any spin adducts), the hexachloroosmate(V) salt (used in very small amounts) will be consumed in a very fast reaction (probably diffusion-controlled) with Bu$_3$N, compared with that with PBN. This aspect will be a further studied later. Benzotriazole, 1,2,3-1H-triazole and 1H-tetrazole, which are difficult to oxidize in their neutral forms, are presumably not oxidized at all by OsCl$_6^-$ in competition with PBN and thus give spin adducts not only from PBN$^{\cdot +}$ but also from 4-NO$_2$PBN$^{\cdot +}$, available only at an approximatively 0.4 V higher potential than PBN$^{\cdot +}$.

Experimental

Chemicals. Tetraphenylphosphonium hexachloroosmate(V) was prepared by PbO$_2$ oxidation of the hexachloroosmate(IV) salt in acetonitrile.[1] Ionic nucleophiles were used as tetrabutylammonium salts, available either commercially or from earlier studies.[21] The tetrabutylammonium hydrogendicarboxylates were prepared by the method earlier given for the hydrogendiacetate salt[3,29] and recrystallized from ethyl acetate. The spin traps, PBN and its 4-nitro derivative, were purchased from Aldrich Co.

Reference compounds were available from either earlier work [**1a,b** and **2**,[10] expected coupling products from the Os(V)/*tert*-butylethoxycarbonylacetate[11]] or prepared by known methods (benzyl phenylacetate[30] and 1,2-dichlorocyclohexane[31]). Reference gases (CH_4, C_2H_6, CH_3Cl, CF_3H, C_2F_6, CF_3Cl and CF_3I) were obtained from commercial sources. Acetonitrile (UVASOL, Merck) was dried and stored over 3 Å molecular sieves. Dichloromethane (Merck, *zur Rückstandsanalyse*) was used as received.

Analyses. GLC was performed by a Varian 1400 gas chromatograph equipped with an HP 3380A integrator on a $2\,m \times 3\,mm$ 5% NPGS on Chromosorb Q or Porapac P 80/100 column or an HP 5890 Ser. II gas chromatograph equipped with an HP 3396 Ser. II integrator on a 25 m fused silica column (OV 1701). Products were, in most cases, identified by comparison of retention times and mass spectra (Finnigan 4021 mass spectrometer) with those of authentic speciments. Yields and product distributions were determined by GLC, using bimesitylene or 1-naphthonitrile as internal standards and calibrated against authentic samples.

Product studies were carried out for the reaction between the hexachloroosmate(V) salt and either tetrabutylammonium carboxylates (trifluoroacetate, phenylacetate) or hydrogendicarboxylates [*tert*-butylcyanoacetate, *tert*-butyl(ethoxycarbonyl)acetate, acetate].

tert-Butylcyanoacetate or phenylacetate. Solutions of the carboxylate salt (0.1–2.0 M) and Ph_4POsCl_6 (20–400 mM) in dichloromethane or acetonitrile were mixed and allowed to react until the color changed to yellow. The solution was worked up by addition of sodium hydrogencarbonate and water, followed by extraction by diethyl ether. Runs with the most concentrated solutions gave the highest yields.

tert-Butylethoxycarbonylacetate. Solutions of the carboxylate salt (final concentration 75 mM) were reacted with solutions of Ph_4POsCl_6 (final concentration 75 mM) in dichloromethane. Blind experiments without the oxidant were made to identify the product peaks in the GLC analyses.

Trifluoroacetate. The reaction was carried out in an argon filled vessel (4 ml) with a gas-tight rubber serum cap. The Ph_4POsCl_6 sample was placed in the vessel before sealing it, and a dichloromethane or acetonitrile solution of the acetate was then injected through the septum. The amount of solvent was kept as small as possible to get as high a salt concentration as possible (~ 1 M) and to dissolve as little as possible of the gases formed. The gas phase was analyzed for products by GLC–MS. A GLC calibration curve was made up for CF_3Cl and used for quantitative analysis.

Acetate. The experiment was performed as for trifluoroacetate. The highest yields of products were obtained at a hydrogendiacetate concentration of 1 M in dichloromethane. The molar ratio of hydrogendiacetate to Ph_4POsCl_6 was varied between 1 and 25, a ratio of 5 being the lower limit for obtaining reasonable yields. No products were detected in the liquid phase.

Tributylamine in tetrabutylammonium salts. A weighed amount of the tetrabutylammonium salt was stirred at room temperature with a known volume of absolute diethyl ether. The ether phase was analyzed for tributylamine by GLC (HP 5890, OV-1701 column, injection volume 2 µl). The peak area was then compared with those from analyses of samples containing known amounts of tributylamine in diethyl ether. The detection limit was 0.2 mM.

In this way it was found that the extraction with the first portion of diethyl ether removed 0.1 % tributylamine from tetrabutylammonium chloride whereas the second portion removed less than 0.01 %. This demonstrated that the GLC peak originated from tributylamine and not from thermal decomposition of any dissolved tetrabutylammonium chloride in the gas chromatograph.[32] In the same way it was found that two extractions removed successively 0.5 and 0.1 % of tributylamine from tetrabutylammonium fluoride, whereas tetrabutylammonium hydrogendiacetate did not contain any detectable amount of tributylamine.

Chloride. The reaction between Ph_4POsCl_6 and Bu_4NCl in acetonitrile was tested for the presence of chlorine by removing the gas phase from the vial by a gas-tight syringe and bubbling it through 100 µl of cyclohexene which was then analyzed by GLC–MS.

Kinetics. Kinetic measurements were made spectrophotometrically in acetonitrile, monitoring the decay of Os(V) at 500 nm. The temperature was kept at 20.0(2)°C (except for the fastest reactions which were run at ~ 23°C). Slow kinetics was followed by means of a Hewlett-Packard 8452A spectrophotometer, equipped with an HP 89500 UV–VIS ChemStation. Moderately rapid reactions (up to $\sim 20\,min^{-1}$) were studied by the stopped-flow method, using a Rapid Kinetics Spectrometer Accessory RX-1000 from Applied Photophysics Ltd., England, in conjunction with the spectrophotometer above. Fast kinetics was followed by the stopped-flow method, using a Hi-Tech SF-3L instrument with an SF 3C Control Unit and Hi Tech 1S-2 software.

Cyclic voltammetry. This was run on ~ 1 mM solutions of PBN or 4-NO_2PBN in acetonitrile/tetrabutylammonium hexafluorophosphate (0.1 M), using the BAS-100 instrument. The anode was a Pt button and the cathode at Pt wire. Irreversible E_{pa} were obtained at 1.53 V (PBN) and 1.91 V vs. Ag/AgCl, or 1.73 and 2.11 V vs. NHE, at a sweep rate of 200 mV s^{-1}.

Electron spin resonance spectra were recorded on a Bruker ER-200D SRC instrument. The spin trapping experiments were performed under the same conditions as described previously[21] for the oxidant, tris(4-bromophenyl)-aminium hexachloroantimonate, except that solid Ph_4POsCl_6 (~ 1 mg) was added to the deoxygenated solution of spin trap and nucleophile.

Various attempts were made to identify the origin of the weak 3×2 signal ($a^N = 1.46$, $a^H = 0.22$ mT) which resulted after the acetoxyl spin adduct had decayed in dichloromethane. It was easily shown that the methyl spin adduct, generated by air oxidation of the addition product between methyllithium and PBN[33] and transferred to an identical medium ($a^N = 1.52$ and $a^H = 0.334$ mT) could not cause the signal, and it was instead suggested[12] that it might be due to $HOCOCH_2$-PBN. Following a published procedure[19] we tried to generate this spin adduct by photolysis of solutions of chloro- or bromo-acetic acid/PBN under a variety of conditions. These experiments were made by photolysis (UV lamp) of solutions (~ 0.1 M) of the appropriate halogen compound and PBN for 2 min. Weak signals were recorded [reactant system/a^N (mT)/a^H (mT)]: $ClCH_2COOH/CH_2Cl_2$, 1.35, 0.178; $ClCH_2COOH$/toluene, 1.47, 0.29; $ClCH_2COOH$ (50% neutralized by Bu_4NOH)/benzene, 1.45, 0.295 (immediately after irradiation), 1.52, 0.43 (after 20 min in the dark); $BrCH_2COOH$/benzene, 1.46, 0.295. PBN/dichloromethane in itself upon the same treatment gave rise to a spin adduct signal with $a^N = 1.44$ and $a^H = 0.26$ mT. Considering the uncertain nature of these results, further attempts at identification were discontinued.

The CF_3-PBN adduct was made in dichloromethane as described[19] and had $a^N = 1.42$, $a^H = 0.188$ and $a^F = 0.147$ mT.

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