Electron Transfer Reactions. XIX.* Outer-Sphere Electron Transfer Reactions between Hexachloroosmate(V) and Organic Compounds

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The reaction between tetraphenylphosphonium hexachloroosmate(V), a strong one-electron oxidant, and typical organic electron transfer reagents has been studied by preparative, kinetic and theoretical methods. Like tungsten hexachloride, hexachloroosmate(V) supports characteristic oxidative nuclear and/or side-chain acetoxylation of aromatic compounds in the presence of an acetate ion source. With tetramethylstannane, the reaction is first order in both reagents and shows no dependence on [(AcO)$_2$H$^-$], the acetate ion source employed in this study. For 4-methoxytoluene (PMT) and naphthalene (Naph), first-order behavior in [OsCl$_6^-$] and [substrate] is observed, whereas reaction orders of 1.4 and 0.5–0.7 in [(AcO)$_2$H$^-$] and −1.0 and −0.5 in [OsCl$_6^{2-}$]$_x$, respectively, indicate that back electron transfer competes with base/nucleophile capture of the intermediate radical cation in a mechanism involving initial, reversible electron transfer followed by a rate-determining follow-up reaction of the radical cation. This is supported in the 4-methoxytoluene case by a strong kinetic deuterium isotope effect upon the measured rate parameter, k_H/k_D being 4.1(2) which is normal for this reaction type. The electron transfer rate constants for the three substrates were evaluated (tetramethylstannane 10.1, 4-methoxytoluene 16 and naphthalene 5.3 M^{-1} s^{-1}) and compared with values calculated by the Marcus treatment. With the assumption that the self-exchange reorganization energies, λ(PMT$^+$·/PMT) and λ(Naph$^+$·/Naph), are high, 50 and 30 kcal mol^{-1}, respectively, the agreement is satisfactory.

A new octahedral complex ion of osmium(V), OsCl$_6^-$, has recently been prepared and characterized.[2–5] This ion was found to be inert towards substitution and to behave as a strong one-electron oxidant towards a range of inorganic and organic substrates. It had an $E°$ of 1.48 V vs. the normal hydrogen electrode (NHE) in acetonitrile and cyclic voltammetry indicated perfectly reversible behavior, with a 60 mV peak-to-peak separation at 50 mV s^{-1}. The OsCl$_6^-$/OsCl$_6^{2-}$ couple is a member of a series of 4d- and 5d-hexachlorometallate complexes which display an orderly progression of redox behavior[5] that so far has not been exploited to any great extent for reactions with organic compounds. Magnuson[3] suggested that an outer-sphere electron-transfer (ET) mechanism is implicated for the reactions of hexachloroosmate(V) with organic molecules, but no experimental evidence was given.

A related compound is tungsten(VI) hexachloride, capable of effecting rapid oxidative acetoxylation of a range of aromatic compounds.[6] It is, however, sensitive to solvolysis, leading to serious interference from concurrent oxidative chlorination. This precludes accurate kinetic studies of the redox behavior of tungsten hexachloride.[6] In view of the higher stability of the hexachloroosmate(V) ion

towards substitution, it would reasonably be expected to be a better model reagent for ET reactions with suitable organic substrates. This investigation deals with the reaction between tetraphenylphosphonium hexachloroosmate(V) and some model organic compounds, in particular tetramethylstannane, 4-methoxytoluene and naphthalene, using product and kinetic studies in combination with the Marcus theory to probe the ET behavior of hexachloroosmate(V). The two former systems were chosen on account of their well-known ET properties.[7–12]

Results

Product studies. These were carried out for naphthalene, 4-methoxytoluene, anisole and mesitylene at ambient temperature with argon protection (Table 1). The solvent was either 90/10 (v/v) dichloromethane/HOAc or acetonitrile/HOAc, acetic acid being added to prevent an otherwise rapid reaction between hexachloroosmate(V) and (AcO)$_2$H$^-$, producing hexachloroosmate(IV) (see below). This strong dampening effect of an excess of acetic acid upon the nucleophilic reactivity of the hydrogendiacetate ion is known from other systems.[1,13] With 10 % acetic acid present the background reaction between hexachloroosmate(V) and acetate ion was slow (second-order rate constant ca. 0.010 M^{-1} s^{-1}; under our actual conditions the

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*Part XVIII, see Ref. 1.
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Table 1. Products (ArX and/or ArCH$_2$X[a]) formed in the oxidative substitution of aromatic compounds by hexachloroosmate(V) in dichloromethane/HOAc (90/10 v/v) or acetonitrile/HOAc (90/10 v/v) at room temperature.

Substrate	Solvent	Reaction time/min	Added component	Yield (%)[a]	
				Acetoxylation	Chlorination
Naphthalene	CH$_2$Cl$_2$	150	NaOAc	34[b]	8
Naphthalene	CH$_2$Cl$_2$	<5	TBA$^+$(AcO)$_2$H$^-$ [c]	56[b]	2
Naphthalene	CH$_2$Cl$_2$[d]	<5	TBA$^+$(AcO)$_2$H$^-$	4[b]	1
Naphthalene	CH$_3$CN	<5	TBA$^+$(AcO)$_2$H$^-$	61[b]	2
Naphthalene	CH$_3$CN[c]	<5	TBA$^+$(AcO)$_2$H$^-$	11[b]	1
Anisole	CH$_2$Cl$_2$	5	TBA$^+$(AcO)$_2$H$^-$	54[e]	1
Mesitylene	CH$_2$Cl$_2$	20	TBA$^+$(AcO)$_2$H$^-$	5[f]	1
Mesitylene	CH$_2$Cl$_2$		TBA$^+$Cl$^-$ (0.1)	0.3	84
Mesitylene	CH$_2$Cl$_2$		TBA$^+$Cl$^-$ (0.05) TBA$^+$(AcO)$_2$H$^-$ (0.05)	2.5	60
PMT	CH$_3$CN	<5	TBA$^+$(AcO)$_2$H$^-$	31[g]	

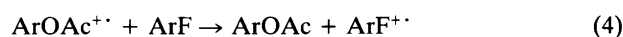[a]Calculated on the basis of 2 mol OsCl$_6^-$ per mole ArX formed. [b]α/β ratio > 1000. [c]TBA$^+$ = tetrabutylammonium ion. [d]Without acetic acid. [e]*ortho/para* ratio 0.6. [f]Nuclear to side-chain ratio 0.4. [g]Nuclear to side-chain ratio 0.24. Ca. 2 % of the aldehyde was also detected.

pseudo-first-order rate constant was in the range 0.01–0.03 min^{-1}) and negligible compared with the substrate reactions.

The products obtained were of the usual nuclear and/or side-chain acetoxylation type, known[14] from many other oxidative substitution studies. The isomer distributions were similar to those observed for tungsten hexachloride and 12-tungstocobaltate(III)-promoted acetoxylations (given in that order within parentheses); o/p ratio from anisole 0.6 (0.52;1.3), α/β ratio from naphthalene >1000 (>350;99) and nuclear to side-chain ratio from PMT 0.6 (0.25; <0.01). These ratios are somewhat different from those obtained in the anodic acetoxylation in acetic acid (2.3, 24, 0.04). Minor amounts of chlorination products were also detected, the chlorine source presumably being the hexachloroosmate ion in either of its oxidation states. Addition of a chloride ion source drastically increased the yield of chlorination products(s).

Product yields were slightly higher in acetonitrile and the stability of hexachloroosmate(V) was also higher and this solvent was therefore used in the kinetic experiments. Reaction times varied with the ease of oxidation of the substrates, as represented by their $E°$ values, mesitylene (2.35 V) > anisole (2.15 V) > naphthalene (2.08 V) > PMT (1.82 V) (Table 1). The long reaction period, 2.5 h, for the first reaction of Table 1 was presumably due to the low solubility of sodium acetate in the medium employed (heterogeneous system). With tetrabutylammonium hydrogendiacetate present the system was homogeneous and this salt was therefore used as the source of base/nucleophile in the kinetic studies.

The S$_{ON}$2 radical cation chain mechanism,[15–18] as typified by oxidatively induced fluorine/acetoxy exchange of fluoroarenes [eqns. (1)–(4)] is considered a diagnostic for ET

$$ArF \rightarrow ArF^{+\cdot} + e^- \tag{1}$$

$$ArF^{+\cdot} + AcO^- \rightarrow \dot{A}r(OAc)F \tag{2}$$

$$\dot{A}r(OAc)F \rightarrow ArOAc^{+\cdot} + F^- \tag{3}$$

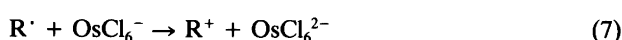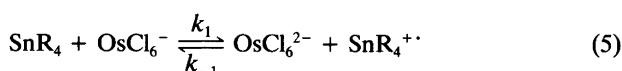$$ArOAc^{+\cdot} + ArF \rightarrow ArOAc + ArF^{+\cdot} \tag{4}$$
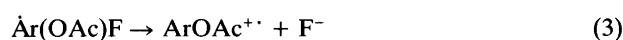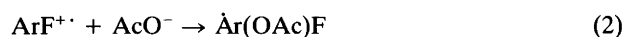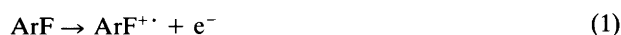
mechanisms, and we therefore made hexachloroosmate(V) react with two known substrates for this reaction, 2-fluoronaphthalene and 4-fluoroanisole. 2-Fluoronaphthalene gave ca. 0.5 % α-naphthyl acetate, the product of the S$_{ON}$2 process, and predominantly (20–25 %) 4-fluoro-2-acetoxynaphthalene, the oxidative acetoxylation product. Similarly, for 4-fluoroanisole the oxidative acetoxylation products, 2-acetoxy-4-fluoroanisole (41 %) and 3-acetoxy-4-fluoroanisole (0.5 %), strongly dominated over the S$_{ON}$2 product, 4-acetoxyanisole (0.9 %). In addition, both substrates gave several other minor products formed via the oxidative substitution pathway.

Cyclic voltammetry. We confirm that the OsCl$_6^-$/OsCl$_6^{2-}$ couple is electrochemically reversible, with $E° = 1.40$ V vs. NHE, 60 mV peak-to-peak separation in acetonitrile/Bu$_4$NPF$_6$ (0.1 M) at a sweep rate of 50 mV s^{-1}. Under similar conditions (acetonitrile, 0.1 M in Et$_4$NClO$_4$) Magnuson[3] obtained 1.48 V (1.24 V vs. SCE, corrected to NHE by the usual conversion factor, 0.24 V). In view of this difference, we measured the $E°$ value with different supporting electrolytes and found 1.46 V in acetonitrile/NaClO$_4$ (0.1 M), 1.43 V in acetonitrile/Et$_4$NBF$_4$ (0.1 M) and 1.44 V in acetonitrile/Et$_4$NClO$_4$ (0.1 M). While these differences are small, they, nevertheless, are indicative of a cation effect upon the reversible potentials of negatively charged ions.[12] This is much stronger in cases where both ions are multiply charged.[19]

Upon addition of 1.2 mM Bu$_4$N[(AcO)$_2$H] to 1.6 mM solution of (Ph$_4$N)$_2$OsCl$_6$ in acetonitrile/Bu$_4$NPF$_6$ (0.1 M), the cyclic voltammogram changed in a way indicative of a

rapid chemical follow-up reaction, giving an i_{pc}/i_{pa} ratio of 0.5 at a sweep rate between 25 and 50 mV s^{-1}. Assuming that the follow-up reaction is irreversible, its second-order rate constant was estimated[20] to be about 10^2 M^{-1} s^{-1}. When the same experiment was repeated in 90/10 (v/v) acetonitrile/HOAc/Bu$_4$NPF$_6$ (0.1 M), no significant changes were seen in the cyclic voltammograms even upon addition of an excess of Bu$_4$N[(AcO)$_2$H$^-$] over the hexachloroosmate salt.[1,13] The reaction between OsCl$_6^-$ and hydrogendiacetate ion in acetonitrile was a redox reaction, giving a quantitative yield of OsCl$_6^{2-}$ (UV/VIS spectroscopy).

Kinetic experiments. All runs were performed under pseudo-first-order conditions, the [substrate]/[OsCl$_6^-$] ratio always being > 8. The absorbance of OsCl$_6^-$ was monitored at its 500 nm maximum in acetonitrile/HOAc (90/10). Tetramethylstannane was chosen as the first substrate in view of its well demonstrated outer-sphere ET behavior toward Fe(III) complexes.[7,8] As in this case, we can assume that ET is followed by a very fast carbon–tin bond cleavage of the radical cation, making the process essentially irreversible [eqns. (5) and (6)]. Table 2 shows pseudo-first-

$$SnR_4 + OsCl_6^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} OsCl_6^{2-} + SnR_4^{+\cdot} \tag{5}$$

$$SnR_4^{+\cdot} \overset{k_2}{\rightarrow} SnR_3^+ + R^{\cdot} \tag{6}$$

$$R^{\cdot} + OsCl_6^- \rightarrow R^+ + OsCl_6^{2-} \tag{7}$$

order rate constants for the reaction between hexachloroosmate(V) and tetramethylstannane, demonstrating that the rate is independent of $[OsCl_6^{2-}]_\infty$ and first order in $[Sn(CH_3)_4]$ (Fig. 1). Added hydrogendiacetate ion had no influence on the rate constant. These observations are in

Table 2. Rate constants for the reaction between hexachloroosmate(V) and tetramethylstannane in acetonitrile/HOAc (88.4/11.7 w/w) at 20.0 °C.

[OsCl$_6^-$]/mM	[Sn(CH$_3$)$_4$]/mM	[(AcO)$_2$H$^-$]/mM	k_{obs}/min^{-1}	k_1/M^{-1} s^{-1} [a]
0.075	2.38	0	2.95	10.3
0.075	2.38	0	2.97	10.4
0.075	2.38	1.2	2.96	10.4
0.075	2.38	2.9	2.84	9.9
0.075	2.38	2.9	2.71	9.5
0.075	2.38	2.9	2.74	9.6
0.15	2.38	0	2.97	10.4
0.30	2.38	0	2.83	9.9
0.075	2.98	0	3.83	10.7
0.075	2.68	0	3.37	10.5
0.075	2.09	0	2.54	10.1
0.075	1.79	0	2.24	10.4
0.075	1.49	0	1.82	10.2
0.075	1.19	0	1.38	9.7
0.075	0.89	0	1.02	9.6

[a]Calculated as $k_{obs}/(2[Me_4Sn])$. See eqns. (5)–(7); $k_{-1} = 0$. The average value of k_1 is 10.1(4) M^{-1} s^{-1}.
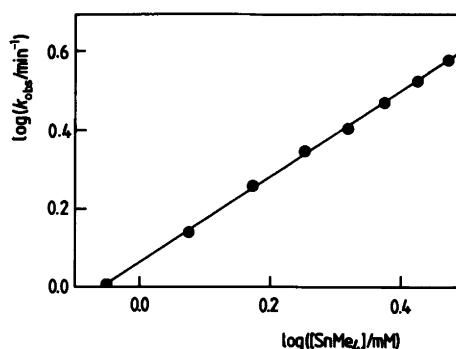
Fig. 1. Plot of log (k_{obs}/min^{-1}) vs. log ([Me$_4$Sn]/mM). The slope of the regression line is 1.09(4).

line with the reaction scheme of eqns. (5) and (6), with the k_1 step rate-determining and $k_2 \gg k_{-1}[OsCl_6^{2-}]$. Thus $k_1 = k_{obs}/(2[Me_4Sn])$ can be estimated to be 10.1(4) M^{-1} s^{-1}.

PMT has also been used as a model organic ET reagent[9–12] and found to follow an ECE type mechanism in its reactions with metal ion reagents, with proton transfer from the radical cation to a base, B:, as the rate-determining step [eqns. (8) and (9)]. The same mechanism was
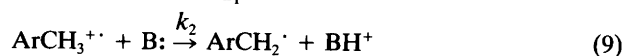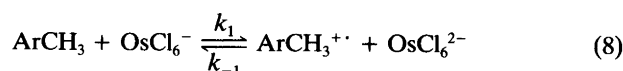
$$ArCH_3 + OsCl_6^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArCH_3^{+\cdot} + OsCl_6^{2-} \tag{8}$$

$$ArCH_3^{+\cdot} + B: \overset{k_2}{\rightarrow} ArCH_2^{\cdot} + BH^+ \tag{9}$$

Table 3. Rate parameters [P(2)] for the reaction between hexachloroosmate(V) and 4-methoxytoluene (PMT) in acetonitrile/HOAc (88.4/11.6 w/w) at 20.0 °C.

[OsCl$_6^-$]/mM	Added [OsCl$_6^{2-}$]/mM	[PMT]/mM	[(AcO)$_2$H$^-$]/mM	P(2)/min^{-1} [a]
0.15	–	1.46	5.56	2.84
0.45	–	1.46	5.56	0.89
0.30	–	1.46	5.56	1.28
0.15	0.15	1.46	5.56	1.14
0.30	–	2.85	5.56	2.62
0.30	–	2.18	5.56	1.88
0.30	–	1.75	5.56	1.55
0.30	–	1.17	5.56	1.07
0.30	–	1.46	2.78	0.61
0.30	–	1.46	6.56	2.08
0.30	–	1.46	10.50	3.68
0.30	–	1.46	3.94	0.99
0.15	–	1.46	2.70	1.00
0.15	–	1.46	3.60	1.43
0.15	–	1.46	4.49	1.88
0.15	–	1.46	6.29	3.04
0.15	–	1.46[b]	6.29	0.72
0.15	–	1.46[b]	2.70	0.25
0.30	–	1.46[b]	7.48	0.42
0.30	–	2.18[b]	5.56	0.48
0.30	–	1.46[b]	5.56	0.33[b]

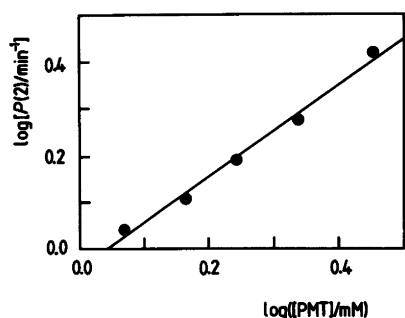[a]Average value of two or more runs in most cases. [b]PMT-d_3.

Fig. 2. Plot of log $[P(2)/\text{min}^{-1}]$ vs. log $([\text{PMT}]/\text{mM})$ at constant $[(\text{AcO})_2\text{H}^-]$ = 5.56 mM. The slope of the regression line is 0.976(4).
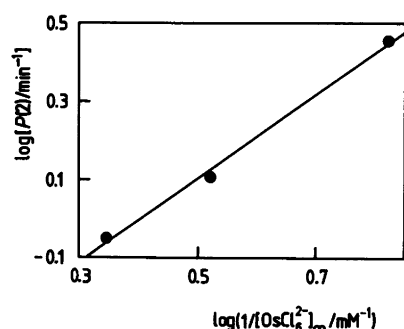

Fig. 4. Plot of log $[P(2)/\text{min}^{-1}]$ vs. log $([\text{OsCl}_6^{2-}]_\infty^{-1}/\text{mM}^{-1})$ at constant [PMT] = 1.46 mM and $[(\text{AcO})_2\text{H}^-]$ = 5.56 mM. The slope of the regression line is 1.0(8).

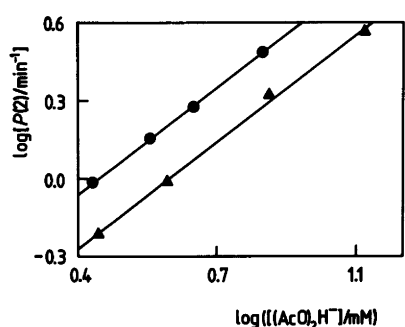*Fig. 3.* Plots of log $[P(2)/\text{min}^{-1}]$ vs. log $\{[(\text{AcO})_2\text{H}^-]/\text{mM}\}$ at constant [PMT] = 1.46 mM and $[\text{OsCl}_6^-]_0$ = 0.15 (circles) and 0.30 (triangles) mM. The slopes of the regression lines are 1.4(1) and 1.4(2), respectively.

found for its reaction with hexachloroosmate(V) (Table 3 and Figs. 2–4). The data were treated in the same way as for the reaction between PMT and 12-tungstocobalt-ate(III),[12] namely by non-linear regression of 200 absorbance (A)/time (t) pairs to eqn. (10), derived for the case in which $[\text{OsCl}_6^-] \ll [\text{ArCH}_3]$ and $[\text{B}] \gg [\text{ArCH}_3^{+\cdot}]$, and with the rate parameter $P(2)$ given by eqn. (11). The range of A values was kept below 0.6, another requirement due to the approximations introduced in the derivation of eqn. (10). This method is discussed in more detail in Ref. 12. The reproducibility of $P(2)$ is shown by the following series of five runs (at $[\text{OsCl}_6^-]_0$ = 0.30 mM, [PMT] = 1.46 mM and $[(\text{AcO})_2\text{H}^-]$ = 5.56 mM): 1.23, 1.27, 1.26, 1.33 and 1.29 min^{-1}.

$$A = \frac{A_\infty + P(1)\exp[-P(2)t]}{1 - P(3)\exp[-P(2)t]} \qquad (10)$$

$$P(2) = \frac{k_1 k_2[\text{PMT}][(\text{OAc})_2\text{H}^-]}{k_{-1}[\text{OsCl}_6^{2-}]_\infty + k_2[(\text{OAc})_2\text{H}^-]} \qquad (11)$$

Fig. 2 shows the dependence of log $P(2)$ on log [PMT], the slope of the regression line being 0.98(1), in good agreement with eqn. (11). The linear relation between

Table 4. Rate parameters $[P(2)]$ for the reaction between hexachloroosmate(V) and naphthalene in acetonitrile/HOAc (88.4/11.6 w/w) at 20.0 °C. $[\text{OsCl}_6^-]_0$ = 0.15 mM.

| [Naph]/mM	$[(\text{AcO})_2\text{H}^-]$/mM	$P(2)$/min^{-1}
1.15	10.8	0.283
1.15[a]	10.8	0.290
1.34	10.2	0.348
1.34	20.0	0.498
1.34	20.3	0.496
1.34	28.8	0.597
1.34	68.2	0.940
1.34	52.8	0.813
2.70	20	1.09
0.80	20	0.263
2.02	20	0.753
3.58	20	1.55
7.16	20	3.01
4.48	20	2.01
11.50	20	4.79
3.49	41.2	2.38
3.49[a]	41.2	2.36
1.75	41.2	1.03
2.79	41.2	2.00
4.19	41.2	2.81
6.99	41.2	5.9
3.49	20	1.54
3.49	10	1.05
3.49	13.6	1.26
3.49	6.8	0.83
3.52[a]	6.8	0.83
3.49	25.02	1.72
3.49	12.04	1.13
3.35	13.54	1.21
3.35	13.89	1.18
3.35	38.63	2.11
3.35	61.25	2.70
3.35	61.75	2.79
3.35	27.90	1.84
6.69	7.26	1.77
6.69	16.26	3.36
6.69	23.52	3.99
6.69	16.35	3.35
6.69	7.02	2.02
6.69	7.26	1.84
6.69	9.91	2.39

[a] Naphthalene-d_8.
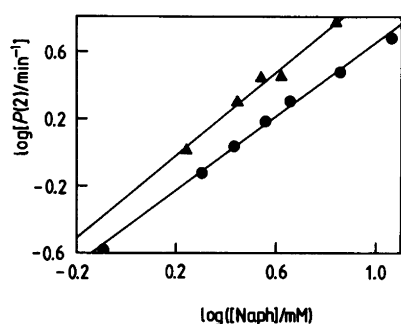
Fig. 5. Plots of log $[P(2)/\text{min}^{-1}]$ vs. log ([Naph]/mM) at constant $[(\text{AcO})_2\text{H}^-]$ = 20.0 (circles) and 41.2 mM (triangles). The slopes of the regression lines are 1.1(1) and 1.2(3), respectively.
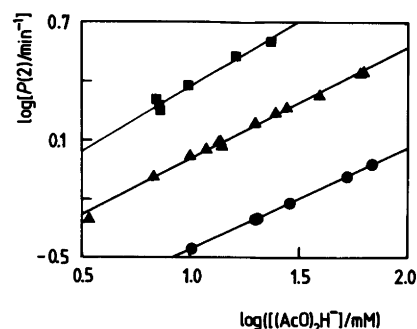

Fig. 6. Plots of log $[P(2)/\text{min}^{-1}]$ vs. log ($[(\text{AcO})_2\text{H}^-]$/mM) at constant [Naph] = 1.34 (circles), 3.42 (average of 3.35 and 3.49; triangles) and 6.69 (squares) mM. The slopes of the regression lines are 0.52(1), 0.57(3), and 0.7(1), respectively.
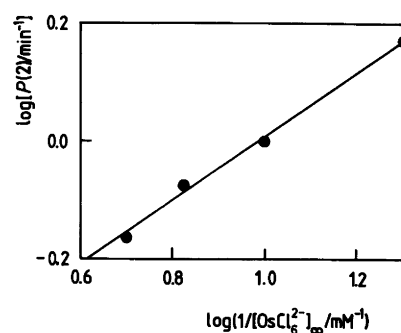
log $P(2)$ and log $[(\text{AcO})_2\text{H}^-]$ is demonstrated in Fig. 3, the slope of the regression line being 1.4(2) for $[\text{OsCl}_6^-]_0$ = 0.15 and 0.30 mM, whereas Fig. 4 shows the inverse first-order behavior of $P(2)$ in $[\text{OsCl}_6^{2-}]_\infty$. Thus the dependence of $P(2)$ in the two latter respects is in reasonable agreement with eqn. (11), assuming that $k_{-1}[\text{OsCl}_6^{2-}]_\infty \gg k_2[(\text{AcO})_2\text{H}^-]$.

From the runs with side-chain-deuteriated PMT (PMT-d_3) kinetic deuterium isotope effects (k_H/k_D) were calculated to be 4.1(2), again in agreement with the assumption that eqn. (9) is rate-determining.

Naphthalene (Naph) has not been investigated kinetically before in this type of reaction. We have assumed that again the reaction is of the ECE type, with a reversible ET step, followed by a rate-determining attack by the nucleophile upon the radical cation, i.e., in principle the same mechanism as that assumed for PMT [eqns. (8) and (9)]. Thus $P(2)$ was determined (Tables 4 and 5) in the same way as for PMT, the reproducibility being indicated by the following series of six runs (at [Naph] = 1.34 mM and $[(\text{AcO})_2\text{H}^-]$ = 20.0 mM): 0.497, 0.512, 0.505, 0.501, 0.486 and 0.487 min^{-1}. $P(2)$ was found to be of the order 1.1(1) and 1.2(3) in [Naph] at $[(\text{AcO})_2\text{H}^-]$ = 20 and 41.2 mM, respectively (Fig. 5), of the order 0.52(2), 0.57(3) and 0.7(1) in $[(\text{AcO})_2\text{H}^-]$ at [Naph] = 1.34, 3.42 and 6.69 mM (Fig. 6), and of the order $-0.5(1)$ in $[\text{OsCl}_6^{2-}]_\infty$ (Fig. 7). The last two reaction orders are not in agreement with eqn. (11), assuming that $k_{-1}[\text{OsCl}_6^{2-}]_\infty \gg k_2[(\text{AcO})_2\text{H}^-]$,

Table 5. Rate parameters $[P(2)]$ for the reaction between hexachloroosmate(V) and naphthalene in acetonitrile/HOAc (88.4/11.6 w/w) at 20.0 °C.

$[\text{OsCl}_6^-]$/mM	$[\text{OsCl}_6^{2-}]$/mM	[Naph]/mM	$[(\text{AcO})_2\text{H}^-]$/mM	$P(2)$/min^{-1}
0.05	–	3.49	6.8	1.48
0.1	–	3.49	6.8	1.00
0.15	–	3.49	6.8	0.84
0.075	0.075	3.49	6.8	0.86
0.1	0.075	3.49	6.8	0.74
0.20	–	3.49	6.8	0.69

Fig. 7. Plot of log $[P(2)/\text{min}^{-1}]$ vs. log ($[\text{OsCl}_6^{2-}]_\infty^{-1}$/mM^{-1}) at constant [Naph] = 3.49 mM and $[(\text{AcO})_2\text{H}^-]$ = 6.8 mM. The slope of the regression line is 0.5(1).

but rather a situation where both these terms influence the kinetics, not unreasonable in view of the very high reactivity of Naph$^{+\cdot}$ toward nucleophiles.[21] No kinetic deuterium isotope effect was found for this substrate (see runs with naphthalene-d_8 in Table 4).

Finally, the ET rate constant k_1 for the hexachloroosmate(V) reaction with PMT and naphthalene was extracted from data of Tables 3 and 4 by plotting $1/P(2)$ vs. 1/[substrate] at constant $[(\text{AcO})_2\text{H}^-]$ (20.0 and 5.56 mM, respectively). The slope then affords $1/k_1$ [see eqn. (11)], giving eventually k_1 = 16(4) and 5.3(5) M^{-1} s^{-1} for PMT and naphthalene, respectively.

Discussion

First we note that hexachloroosmate(V) supports oxidative acetoxylation of naphthalene and PMT, giving products qualitatively resembling a host of other metal-ion-promoted acetoxylation reactions.[14] Quantitatively, its behavior with regard to isomer distribution is closely similar to that of tungsten(VI) hexachloride and 12-tungstocobalt-ate(III) and distinctly different from that of anodic or Ag(II)-promoted acetoxylation. As concluded earlier,[14] these differences in isomer distribution within this family of reasonably well corroborated ET reactions cannot

presently be explained in any satisfactory way, especially since the reactions have been run under widely differing conditions (solvent, temperature and nucleophile concentration).

The hexachloroosmate(V)-promoted acetoxylation of fluoroarenes is by far dominated by conventional oxidative acetoxylation and the $S_{ON}2$ pathway is only a minor one. Insofar as these numbers are known, the ratio between these reaction modes for different oxidants, substrates and conditions are summarized in Table 6, showing that cases of low ratios can be found even for a compulsory ET process, e.g., anodic oxidation of 1-fluoronaphthalene.[24] This was explained in terms of more efficient chain-breaking processes in the layer near the anode, particularly further oxidation of the intermediate fluoroacetoxycyclo-hexadienyl radical formed in eqn. (2). Once the fluoro-acetoxycyclohexadienyl cation is formed, it follows an easy pathway to the oxidative acetoxylation product. An increase in temperature increases the diffusion of the fluoro-acetoxycyclohexadienyl radical into the bulk of the solution, thus favoring the radical cation chain propagation reaction.[24] Applying a similar line of thought to the hexa-chloroosmate(V) system, one might assume that the high oxidizing power of this ion favors further oxidation of the fluoroacetoxycyclohexadienyl radical and thus inhibits the chain reaction. The seemingly contradictory fact that sulfate anion radical, by far the strongest oxidant of Table 6 ($E° = 2.6$ V), does favor the $S_{ON}2$ process, is not relevant since in these experiments sulfate anion radical is formed in very low concentration by thermal decomposition of peroxydisulfate ion. Thus second-order reactions between the fluoroacetoxycyclohexadienyl radical and sulfate radical anion will be extremely slow, both species being transient radicals.

Turning to the kinetic results, we first note that the reaction between hexachloroosmate(V) and tetramethyl-stannane is first order in both reagents, with no detectable effect of reversibility of the ET step. This is entirely in line with the kinetic results on iron(III)phenanthroline/tetra-alkylstannane reactions[7,8] and with the extreme instability of tetraalkylstannane radical cations. For both PMT and

Naph the reversibility of the ET step is reflected in the kinetics, introducing terms involving [base/nucleophile] and $[OsCl_6^{2-}]$ in the anticipated manner. In fact, the behavior of the PMT reaction is closely similar to that of its reaction with 12-tungstocobaltate (III),[12] an archetypal ET reagent.

As a starting point for the discussion of the kinetic results presented above, ET rate constants were calculated for the ET steps involved, using the Marcus treatment[26-28] according to eqns. (12)–(14), where $\Delta G°$ is the free energy

$$\Delta G^{\ddagger} = \lambda(1 + \Delta G°'/\lambda)^2/4 \tag{12}$$

$$\Delta G°' = \Delta G° + (Z_1 - Z_2 - 1)\ 331.2\ f/(D\ r_{12}) \tag{13}$$

$$\log (k_{ET}/M^{-1}\ s^{-1}) = 11 - \Delta G^{\ddagger}/(2.303\ RT) \tag{14}$$

change of the ET step under the prevailing experimental conditions, λ is the reorganization energy, Z_1 and Z_2 are the charges of the two species (approximated as two spheres of radii r_1 and r_2 in an isotropic medium of dielectric constant D), f is a factor describing the influence of ionic strength, $r_{12} = r_1 + r_2$ and R and T have their usual meanings. The results are given in Table 7.

The choice of parameters to be entered into the Marcus model is to some extent dependent on analogies with other systems for which data are known. The reversible potential (denoted $E°$ in Table 7) of $OsCl_6^-/OsCl_6^{2-}$ was found to be 1.40 V by us in both acetonitrile and acetonitrile/HOAc (90/10 v/v), 0.1 M in tetrabutylammonium hexafluorophosphate, whereas Magnuson[3] obtained 1.48 V in acetonitrile/0.1 M tetraethylammonium perchlorate (where we obtained 1.44 V). In view of our choice of a tetrabutylammonium salt as the acetate ion source we selected the value 1.40 V as the lower extreme and 1.48 V as the higher one. The rather low value of 20 kcal mol^{-1} for the $\lambda(0)$ of the $OsCl_6^-/OsCl_6^{2-}$ couple is an estimate, based on the similarity with the $IrCl_6^{2-}/IrCl_6^{3-}$ system (26 kcal mol^{-1}),[30] the almost perfect electrochemical reversibility of the Os(V)/Os(IV) couple and the small structural change in going from the Os(V) to Os(IV) state[4] (lengthening of the Os−Cl

Table 6. $S_{ON}2$ substitution vs. oxidative acetoxylation for a number of oxidants under different conditions.

Substrate	Oxidant	Medium	[AcO⁻]/mM	Temp./°C	Ratio ($S_{ON}2$/oxidative acetox.)
4-F-Anisole	$OsCl_6^-$	AN/HOAc (9/1)	100	20	ca. 0.03[a]
4-F-Anisole	$OsCl_6^-$	AN/HOAc (9/1)	100	60	ca. 0.02[a]
4-F-Anisole	Anode	HOAc	500	25	>50[b]
4-F-Anisole	$Co(III)W_{12}O_{40}^{5-}$	HOAc/H$_2$O (4/1)	100	102	>50[c]
4-F-Anisole	Ag(II)	HOAc	500	20	>50[d]
1-F-Naph	$OsCl_6^-$	AN/HOAc (9/1)	15	20	ca. 0.02[a]
1-F-Naph	Anode	HOAc	500	20	0.043[e]
1-F-Naph	Anode	HOAc	500	78	1.0[e]
1-F-Naph	$SO_4^{-\cdot}$	HOAc	500	110	>20[e]
1-F-Naph	Cu(III)	HOAc	500	110	>80[e]
6-F-BP[f]	$Mn(OAc)_3$	HOAc		40	>100[g]

[a]This work. [b]Refs. 16, 17. [c]Ref. 22. [d]Ref. 23. [e]Ref. 24. [f]BP = benzo[a]pyrene. [g]Ref. 25.

Table 7. Calculation of outer-sphere ET rate constants according to the Marcus treatment for the reactions between hexachloroosmate(V) and tetramethylstannane, 4-methoxytoluene (PMT) and naphthalene (Naph) at 20 °C. No correction for the possible effect of ionic strength was attempted.

Redox pair	$E°/V$	$\lambda(0)/kcal\ mol^{-1}$	Radius/Å	log $(k_{ET}/M^{-1}\ s^{-1})$	
				Calculated	Experimental
$OsCl_6^-/OsCl_6^{2-}$	1.40[a]	20[b]	4.1[c]		
	1.48[d]	20	4.1		
$Me_4Sn^{+\cdot}/Me_4Sn$	1.95[e]	52[e]	4.4[e]	−0.1, 0.7	0.93
	1.90[f]	66[f]	4.4	−0.8, 0.0	
$PMT^{+\cdot}/PMT$	1.82[g]	10[b]	2.0[g]	5.3, 6.2	1.2
	1.82	20[b]	2.0	4.5, 5.3	
	1.82	30[b]	2.0	3.6, 4.4	
	1.82	40[b]	2.0	2.7, 3.5	
	1.82	50[b]	2.0	1.8, 2.6	
	1.82	60[b]	2.0	0.9, 1.7	
$Naph^{+\cdot}/Naph$	2.08[h]	10[b]	2.5[e]	1.5, 2.7	0.73
	2.08	20[b]	2.5	1.0, 2.1	
	2.08	30[b]	2.5	0.4, 1.4	
	2.08	40[b]	2.5	−0.3, 0.6	

[a]This work. [b]Estimated value (see the text). [c]Ref. 5. [d]Ref. 4. [e]Ref. 8. [f]Ref. 28. [g]Ref. 12. [h]Ref. 29.

bond by merely 0.048 Å, corresponding to a low value of λ_i). For the $Me_4Sn^{+\cdot}/Me_4Sn$ couple the two sets of $E°/\lambda(0)$ reflect differing computational methods for their extraction from the same body of experimental data, whereas for PMT and naphthalene the chosen variation in $\lambda(0)$ reflects some new insights recently obtained with regard to the $\lambda(0)$ values of $ArCH_3^{+\cdot}/ArCH_3$ couples (see below). We did not attempt to include the effect of ionic strength in the calculations of the electrostatic terms, mainly because of the insensitivity of the tetramethylstannane rate constants to ionic strength (Table 2) which indicates that this effect is small.

There is strong experimental support for the outer-sphere nature of the ET step between a tetraalkylstannane and Fe(III)phenanthroline complexes, among others manifested by a high degree of adherence of log $(k_{ET})/\Delta G°'$ data to the Marcus theory,[8] irrespective of the steric requirements of the tetraalkylstannane. Thus in going from tetramethyl- to tetraneopentylstannane, only $E°$ influenced the ET rate constant. Our finding that the Marcus treatment calculates k_{ET} fairly well for the reaction between hexachloroosmate(V) and tetramethylstannane can be taken as a strong indication that the reaction is of the outer-sphere type.

For PMT, the calculation reported in Table 7 gives a much *higher* calculated k_{ET} than the observed value, assuming a *low* $\lambda(0)$ of 10 kcal mol^{-1} for the $PMT^{+\cdot}/PMT$ system.[12] This is an unusual situation; normally deviations from the Marcus theory are in the opposite direction, indicating that the step under study is of the inner-sphere ET or polar type. However, it is not obvious that such a low $\lambda(0)$ value is really pertinent to $PMT^{+\cdot}/PMT$. The original assumption[12] of 10 kcal mol^{-1} was based on the analogy

with $\lambda(0)$ values of unsubstituted aromatics and heteroaromatics which have been determined experimentally and shown to cluster in the region around 10 kcal mol^{-1}. Later developments have changed this view. Table 8 lists measured $\lambda(0)$ for a number of alkylaromatic systems $(ArCH_3^{+\cdot}/ArCH_3)$, determined experimentally via kinetic methods[8,31] (and of course assuming that the Marcus theory can be applied). These $\lambda(0)$ values are high, of the order of 50 kcal mol^{-1}, and from Table 7 one sees that this $\lambda(0)$ gives a much better agreement between theory and experiment. A value of 60 kcal mol^{-1} would give an even better fit, but then we must remember that the effect of ionic strength [which would, if anything, lower the calculated log (k_{ET})] has not been taken into account.

Table 8. Reorganization energies for electron self-exchange between $ArCH_3^{+\cdot}$ and $ArCH_3$ as determined experimentally. $\lambda[Fe^{III}(phen)_3/Fe^{II}(phen)_3]$ was set equal to 14 kcal mol^{-1}.[32]

$ArCH_3$	$\lambda(0)/kcal\ mol^{-1}$	Ref.
Hexamethylbenzene	43, 48	10, 11
	44	31
Pentamethylbenzene	39, 47	10, 11
	44	31
1,2,4,5-Tetramethylbenzene	36, 38	10, 11
	44	31
1,2,3,4-Tetramethylbenzene	40, 59	10, 11
	55	31
1,2,3,5-Tetramethylbenzene	49	31
1,2,3-Trimethylbenzene	55	31
4-Methoxytoluene (PMT)	48	10
	44	31

An analysis of the rate data of the reaction between PMT and 12-tungstocobaltate(III) ion at 50°C in HOAc/water (55/45), 0.47 M in KOAc, shows that the experimental k_{ET}, $1.0(1)\times10^{-2}$ M^{-1} s^{-1} {extracted from data in Table 2 of Ref. 12 by means of a $1/P(2)$–$1/$[PMT] plot}, is now in good agreement with the theoretical value, 3×10^{-2} M^{-1} s^{-1}, using relevant parameters from Ref. 12 and λ(PMT$^{+\cdot}$/PMT) = 50 kcal mol^{-1}.

For calculation of the naphthalene ET rate constant, it is seen (Table 7) that a value of λ(Naph$^{+\cdot}$/Naph) of ca. 30 kcal mol^{-1} gives the best agreement. This is significantly higher than the value one would choose on the basis of $\lambda(0)$ of analogous aromatic and heteroaromatic compounds, ca. 10 kcal mol^{-1} (see Table 7, Ref. 28). It should however be emphasized that these low values are all based on experimentally determined self-exchange ET rate constants which may be influenced by an inner-sphere component to an unknown degree. Certain reactions of radical anions have recently[33] been shown to be of the inner-sphere ET type, thus posing the question of how to assess experimentally derived $\lambda(0)$ values; the existence of similar problems in radical cation chemistry seems likely and may be reflected in the calculations reported above.

Experimental

Chemicals. Ph$_4$POsCl$_6$ was prepared according to the method given by Magnuson.[3] Acetonitrile (Merck, UVASOL®) and dichloromethane (Merck) were dried and stored over 3 Å molecular sieves. Sodium acetate was dried overnight at 120°C and tetrabutylammonium hydrogendiacetate was prepared by dichloromethane extraction of an aqueous solution of tetrabutylammonium hydrogen sulfate and sodium acetate in a 1:2 molar ratio. After evaporation of the dichloromethane, the solid was recrystallized twice from ethyl acetate.[34] PMT was purified by fractionation through a 40-plate column (Fischer Spaltrohr System). PMT-α,α,α-d_3 was prepared according to a literature method.[9] All other chemicals were either of the highest quality commercially available or were prepared according to known methods described in earlier work.[35,36]

Analysis. Gas–liquid chromatography was performed using a Varian 1400 gas chromatograph equipped with an electronic integrator (Hewlett Packard 3380 A) on a 2 m×3 mm 5 % NPGS on Chromosorb W column. Products were identified by comparison of GLC retention times with authentic samples and/or comparison of their mass spectra, recorded on a Finnigan 4021 instrument. Yields and isomer distributions were determined by GLC using 1-naphthonitrile (1-naphthyl acetate in the mesitylene and 4-fluoroanisole experiments, 4-nitroanisole in the anisole experiments, and bimesityl in the 1-fluoronaphthalene experiments) as an internal standard calibrated against authentic samples.

Cyclic voltammetry was performed under argon protection by means of a BAS-100 instrument, using an Ag/AgCl electrode as the reference electrode. The reversible potential of the ferrocene$^{+\cdot}$/ferrocene (FcH) couple was used as the standard for conversion to the NHE scale, assuming that $E°$(FcH$^{+\cdot}$/FcH) is 0.60 V on the latter. We are aware that this value is subject to discussion[37] and that values in the range 0.53–0.72 V have been proposed, but would like to defer a more thorough discussion of this problem to a later date.[19]

Product studies. A solution of Ph$_4$P$^+$OsCl$_6^-$ in the organic solvent, dichloromethane or acetonitrile, was mixed with a solution of the substrate and sodium acetate in glacial acetic acid. This mixture was stirred at room temperature, protected by a slow stream of argon through the vessel, until the color had changed to yellow. When Bu$_4$N(AcO)$_2$H was used as a base/nucleophile, part of the organic solvent was added to the acetic acid solution before addition of the reagent solution. Work-up consisted of sodium hydrogencarbonate neutralization followed by ether extraction [(Bu$_4$N)$_2$OsCl$_6$ is not soluble in ether] and GLC analysis.

Kinetics. All kinetic experiments were run at 20.0 ± 0.1°C in the thermostatted cell compartment of a Cary 219 UV/VIS spectrophotometer, equipped with a digital interface port and connected to an HP-85 microcomputer. The reaction was started by rapid addition of the appropriate OsCl$_6^-$ solution and the absorbance at 500 nm recorded as a function of time, 200 data points being collected automatically at regular intervals and stored on magnetic tape. The data set was then analyzed on an HP-9835 tabletop computer by the non-linear regression method developed by Marquardt.[12,38]

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