Electron Transfer Reactions in Organic Chemistry. XXII.[†] Kinetics and Products of Reactions between Hexachloroosmate(V) and Tetraalkylstannanes and Benzyltrimethylsilanes

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The reaction between tetraphenylphosphonium hexachloroosmate(V) and tetraalkylstannanes and benzyltrimethylsilanes has been studied in order to provide further evidence for its electron-transfer character. All reactions were first order in $[R_4M]$ (M = metal) and $[OsCl_6{}^-]$ and both kinetics and product studies indicated that the mechanism involves an initial, slow and reversible electron-transfer step, followed by very fast cleavage of the radical cation formed. The kinetic data are discussed in terms of the Marcus theory of outer-sphere electron transfer, and it is found that the $OsCl_6{}^-$/benzyltrimethylsilane reactions deviate somewhat from outer-sphere behavior.

Hexachloroosmate(V),[2–6] an octahedral complex ion of osmium(V) with $E°(Os^V/Os^{IV}) = 1.40–1.46$ V vs. the normal hydrogen electrode (NHE) in acetonitrile, somewhat dependent on the nature of the supporting electrolyte,[2] has been found to behave as an outer-sphere oxidant toward a range of inorganic and organic compounds. In a series of papers dealing with metal-ion oxidation of organic compounds, we recently studied the reactions between tetraphenylphosphonium hexachloroosmate(V) and a representative set of compounds, namely naphthalene, anisole, mesitylene, 4-methoxytoluene and tetramethylstannane.[2] In the presence of an acetate ion source, this reagent supports two-electron oxidative nuclear and/or side-chain acetoxylation reactions [eqn. (1)], characteristic of the interaction between oxidant, acetate ion and substrate found in many other cases,

$$ArH(ArCH_3) + AcO^-$$

$$\rightarrow ArOAc(ArCH_2OAc) + H^+ + 2e^- \qquad (1)$$
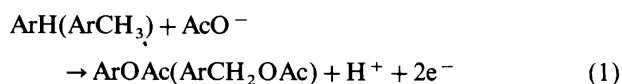
including anodic oxidation.[7–9] Small amounts of chlorination products were also detected from naphthalene, anisole and mesitylene, presumably resulting from the abstraction of a chlorine atom by intermediate neutral radicals from hexachloroosmate(V/IV). The second-order

rate constants agreed fairly well with those calculated by the Marcus theory.[10]

We now report an extension of this study by adding three alkylstannanes, viz., tetraethyl-, tetrapropyl- and tetrabutyl-stannane and four X-benzyltrimethylsilanes (X = H, 3-Cl, 4-CH$_3$ and 4-F). The former class of substrate was chosen in view of its well demonstrated outer-sphere behavior toward iron(III)–phenanthroline complexes.[11] As pointed out by Baciocchi,[12] the benzylsilanes are well suited, as kinetic probes, to electron transfer (ET) reactions, since the corresponding radical cations undergo very fast desilylation, presumably with nucleophilic assistance,[13] and eventually form benzylic derivatives [eqn. (2)]. In polar or free radical reactions, the trimethylsilyl group would, on the other hand, be expected to be retained in the product(s).

$$ArCH_2Si(CH_3)_3 - e^- \rightarrow ArCH_2Si(CH_3)_3{}^{\cdot+}$$

$$\rightarrow ArCH_2{}^\cdot + (CH_3)_3Si^+ \qquad (2)$$
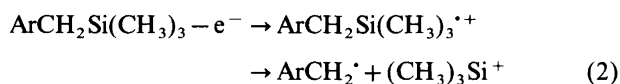
Results

Product studies. These were carried out at ambient temperature for the benzyltrimethylsilanes in acetonitrile/acetic acid (90/10 v/v), protected by an Ar atmosphere. The acetic acid was added in order to prevent the otherwise rapid reaction between hexachloroosmate(V) and tetrabutylammonium hydrogendiacetate $[Bu_4N^+(AcO)_2H^-]$, the acetate ion source used in some

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† Part XXI, see Ref. 1.
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of the experiments. The hydrogendiacetate ion is partly dissociated into acetate ion and acetic acid in acetonitrile [eqn. (3)], and it is acetate ion which is the
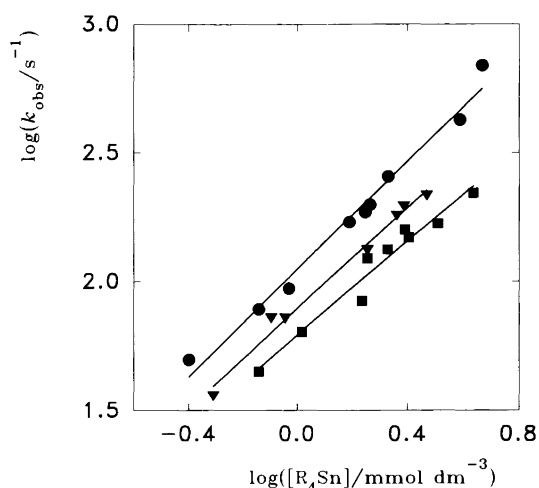
$$(AcO)_2H^- \rightleftarrows AcO^- + AcOH \qquad (3)$$

reactive species toward hexachloroosmate(V) in a redox process.[14] With enough acetic acid present, the formation of acetate ion is completely suppressed and then hexachloroosmate(V) is stable.[15]

Under these conditions, hexachloroosmate(V) and benzyltrimethylsilane in a 1 : 1 or 1 : 2 ratio react to give a mixture of benzyl acetate (2–3%) and benzyl chloride (70–90%). Similar yields and distributions of acetates/ chlorides were obtained from the X-benzyltrimethyl-silanes (X = 3-Cl, 4-CH$_3$, 4-F). The presence of tetrabutylammonium hydrogendiacetate had no significant effect on the product distribution. Runs with an excess of hexachloroosmate (V) showed that 2 equivalents of the oxidant were consumed per R$_4$Si and that OsCl$_6^{2-}$ was the end product.

Tetrabutylstannane and tetraphenylphosphonium hexachloroosmate(V) in a 3 : 1 ratio in acetonitrile reacted to give small amounts of a butene (1.6% yield), 1-chlorobutane (8%) and 2-chlorobutane (~0.5%), as calculated for a two-electron oxidation. A run with an excess of hexachloroosmate(V) showed that 3 equivalents of the oxidant were consumed per Bu$_4$Sn, and that the Os(IV) species first formed was OsCl$_6^{2-}$ but this was

Fig. 1. Plots of log (k_{obs}/s^{-1}) vs. log ([R$_4$Sn]/mM) in acetonitrile/HOAc at 20.0°C. The slopes of the regression lines were 1.04(2) for tetraethylstannane (○), 0.91(7) for tetrapropylstannane (■) and 0.97(5) for tetrabutylstannane (▼). Data, see Table 1.

eventually transformed into a second Os(IV) species with different UV–VIS spectral characteristics. The same was found for Me$_4$Sn.

EPR spectral experiments. Since the product studies indicated that the benzylic chlorides might, at least partially, be formed by a radical mechanism (benzyl radical attack upon a chloroosmate species), attempts were made to trap benzyl radicals by a spin trap,[16] α-phenyl-N-*tert*-butylnitrone (PBN; IUPAC name N-benzylidene-*tert*-butylamine N-oxide, $E_{pa} = 1.75$ V vs. NHE) added to a solution of benzyltrimethylsilane and hexachloro-osmate(V) in acetonitrile or dichloromethane. However, even with a large excess of the silane over PBN in order to compensate for its much lower ET reactivity

Table 1. Rate constants for the reaction between tetraphenylphosphonium hexachloroosmate(V) and tetralkyl-stannanes, R$_4$Sn, in acetonitrile/acetic acid (90/10 v/v) at 20.0°C.

R	[R$_4$Sn]/mM	[OsCl$_6^-$]/mM	k_{obs}/s^{-1}	k/10^4 M^{-1} s^{-1}
Et	0.40	0.075	50	6.3
Et	0.72	0.075	78	5.5
Et	1.77	0.075	186	5.3
Et	2.14	0.075	256	6.0
Et	0.93	0.15	94	5.0
Et	1.55	0.15	170	5.4
Et	1.84	0.15	199	5.4
Et	3.88	0.15	423	5.4
Et	4.65	0.15	688	7.4
Pr	0.72	0.075	45	3.2
Pr	1.04	0.075	64	3.1
Pr	1.80	0.075	123	3.4
Pr	2.13	0.075	133	3.1
Pr	2.46	0.075	159	3.2
Pr	1.72	0.15	84	2.4
Pr	2.54	0.15	148	3.0
Pr	3.23	0.15	168	2.6
Pr	4.33	0.15	221	2.6
Bu	0.49	0.075	36	3.7
Bu	0.80	0.075	72	4.5
Bu	0.90	0.075	72	4.0
Bu	1.80	0.075	132	3.7
Bu	2.30	0.075	180	3.9
Bu	2.44	0.075	196	4.0
Bu	2.95	0.075	216	3.7

Table 2. Rate constants for the reaction between tetraphenylphosphonium hexachloroosmate(V) (0.075 mM) and tetrapropylstannane (1.71 mM) in acetonitrile/acetic acid (90/10 v/v) at 20.0°C.

Bu$_4$N[(AcO)$_2$H]/ mM	k_{obs}/s^{-1}	Average value/s^{-1}	k/10^4 M^{-1} s^{-1}
0.49	103		
0.49	102		
0.49	103	103	3.0
0.81	98		
0.81	111		
0.81	105	107	3.1
1.27	99		
1.27	104		
1.27	106	102	3.0
1.59	108		
1.59	109		
1.59	109	109	3.2
2.06	110		
2.06	108	109	3.2

Table 3. Rate constants for the reaction between tetraphenylphosphonium hexachloroosmate(V) and benzyltrimethylsilane (BTMS) in acetonitrile/acetic acid (90/10 v/v) at 20.0°C.

[BTMS]/ mM	[OsCl$_6$$^-$]/ mM	[(AcO)$_2$H$^-$]/ mM	k_{obs}/min^{-1}	k_2/M^{-1} s^{-1}	$k_{average}$/ M^{-1} s^{-1}
3.33	0.30	2.97	3.17	7.9	
3.33	0.23	2.97	3.15	7.9	
3.33	0.15	2.97	3.11	7.8	
3.33	0.08	2.97	3.27	8.2	8.0
3.39	0.15	6.21	3.50	8.6	
3.39	0.15	5.63	3.42	8.4	
3.39	0.15	3.02	3.25	8.0	
3.39	0.15	2.78	3.31	8.1	
3.39	0.15	1.21	3.35	8.2	8.3
1.32	0.15	—	1.38	8.7	
1.80	0.15	—	1.87	8.7	
2.23	0.15	—	2.39	8.9	
2.49	0.15	—	2.16	7.2	
2.97	0.15	—	2.63	7.4	
3.39	0.15	—	3.18	7.8	
4.51	0.15	—	4.95	9.2	
5.67	0.15	—	5.10	7.5	
6.97	0.15	—	6.50	7.8	8.1

($E^\circ = 2.06$ V vs. NHE) only the characteristic EPR signal of PhCON(-O$^\bullet$)Bu$'$ (a commonly observed oxidation product of PBN; $a^N = 0.80$ mT[16b]) was observed.
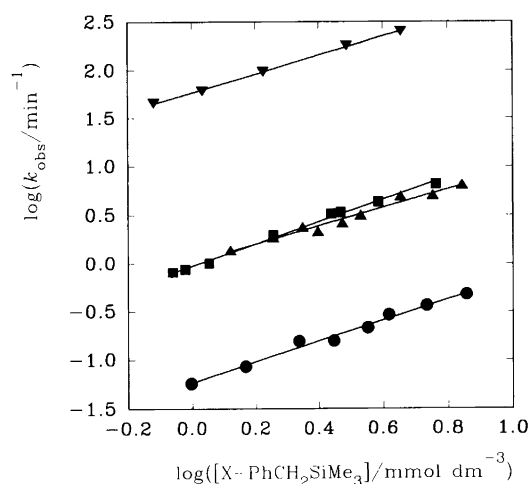
Kinetic experiments. The pseudo-first-order rate constants for reaction between hexachloroosmate(V) and tetraethyl-, tetrapropyl- and tetrabutyl-stannanes in acetonitrile/acetic acid (90/10 v/v) at 20.0°C are shown in Table 1. The rate constant was independent of [OsCl$_6$$^{2-}$]$_\infty$ and first order in [R$_4$Sn] (Fig. 1), as previously observed for tetramethylstannane. Tetra-

Table 4. Rate constants for the reaction between tetraphenylphosphonium hexachloroosmate(V) (0.15 mM) and X-benzyltrimethylsilanes (X-BTMS) in acetonitrile/acetic acid (v/v) at 20.0°C.

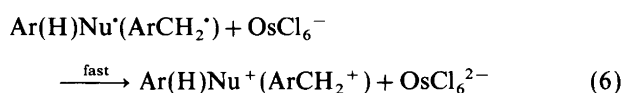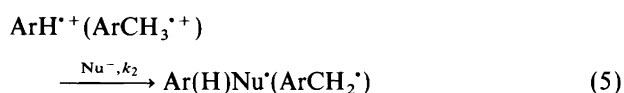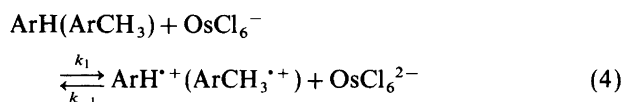| X	[X-BTMS]/ mM	k_{obs}/min^{-1}	k_2/M^{-1} s^{-1}	k_2(average)/ M^{-1} s^{-1}
3-Cl	0.99	0.057	0.48	
	1.47	0.085	0.48	
	2.17	0.156	0.60	
	2.79	0.157	0.47	
	3.56	0.214	0.50	
	4.14	0.293	0.59	
	5.42	0.364	0.56	
	7.19	0.477	0.55	0.53
4-CH$_3$	0.76	45.6	500	
	1.08	61.1	472	
	1.68	97.0	481	
	3.07	179.4	487	
	4.53	251	462	480
4-F	0.87	0.807	7.7	
	0.95	0.866	7.6	
	1.13	1.01	7.4	
	1.80	1.98	9.2	
	2.74	3.27	10.0	
	2.93	3.38	9.6	
	3.85	4.31	9.3	
	5.79	6.59	9.5	8.8

isopropyl- and tetraneopentyl-stannane were also studied but reacted too rapidly for our kinetic method (stopped-flow technique) to be usable, as expected on the basis of their lower redox potentials for one-electron oxidation.[11b] Thus their rate constants could be estimated to be $> (1-2) \times 10^6$ M^{-1} s^{-1}. Added tetrabutylammonium hydrogendiacetate had no effect on the rate constants, as studied with tetrapropylstannane (Table 2). The second-order rate constants k_2 were given as $k_{obs}/(2[\text{substrate}])$ (see below).

Rate constants for the X-benzyltrimethylsilanes are shown in Tables 3 and 4. Again, no effect due to hydrogendiacetate was detected, nor was any influence of [OsCl$_6$$^{2-}$]$_\infty$ found. The reactions were first order in [substrate] (Fig. 2).

Fig. 2. Plots of log (k_{obs}/s^{-1}) vs. log ([X-PhCH$_2$SiMe$_3$]/ mM) in acetonitrile/HOAc at 20.0°C. The slopes of the regression lines were 0.94(6) for X = H (▲), 0.97(2) for X = 4-CH$_3$ (▼), 1.15(4) for X = 4-F (■) and 1.08(5) for X = 3-Cl (●). Data, see Tables 3 and 4.

Discussion
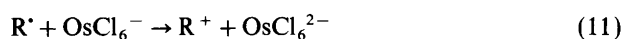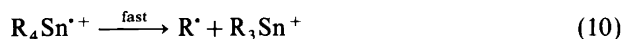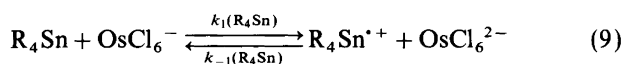
We have earlier[2] analyzed the kinetics of the oxidative acetoxylation of naphthalene and 4-methoxytoluene by $OsCl_6^-$ in terms of an ECEC-type mechanism [eqns. (4)–(7)], comprising an initial reversible ET step,

$$ArH(ArCH_3) + OsCl_6^-$$

$$\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArH^{\cdot +}(ArCH_3^{\cdot +}) + OsCl_6^{2-} \qquad (4)$$

$$ArH^{\cdot +}(ArCH_3^{\cdot +})$$

$$\xrightarrow{Nu^-, k_2} Ar(H)Nu^{\cdot}(ArCH_2^{\cdot}) \qquad (5)$$

$$Ar(H)Nu^{\cdot}(ArCH_2^{\cdot}) + OsCl_6^-$$

$$\xrightarrow{fast} Ar(H)Nu^+(ArCH_2^+) + OsCl_6^{2-} \qquad (6)$$

$$Ar(H)Nu^+(ArCH_2^+)$$

$$\xrightarrow{fast, Nu^-} Ar-Nu(ArCH_2Nu) \qquad (7)$$

followed by (i) a chemical step (formation of an acetoxycyclohexadienyl radical or proton loss) and (ii) a second electron-transfer step. A second chemical step completes the transformation into the nuclear/side-chain acetoxylation product. The kinetics were of the type expected for an initial fast ET step, followed by a slow chemical step (k_2) and analyzed by determining the composite parameter, $P(2)$, shown in eqn. (8).

$$P(2) = \frac{k_1 k_2 [\text{substrate}][Nu^-]}{k_{-1}[OsCl_6^{2-}]_\infty + k_2[Nu^-]} \qquad (8)$$

The reaction between tetramethylstannane and $OsCl_6^-$ exhibited less complex kinetics, indicating that the step following electron transfer was irreversible owing to very rapid cleavage of one Sn–C bond in the stannane radical cation.[11a,b] Thus the rate constant of the electron transfer step, $k_1(Me_4Sn)$, could be put equal to the observed pseudo-first-order rate constant, k_{obs}, divided by $2[Me_4Sn]$, the factor 2 originating from an assumption that the methyl radical formed in the chemical step would consume a second $OsCl_6^-$ [eqns. (9)–(11), R = Me].

$$R_4Sn + OsCl_6^- \underset{k_{-1}(R_4Sn)}{\overset{k_1(R_4Sn)}{\rightleftharpoons}} R_4Sn^{\cdot +} + OsCl_6^{2-} \qquad (9)$$

$$R_4Sn^{\cdot +} \xrightarrow{fast} R^{\cdot} + R_3Sn^+ \qquad (10)$$

$$R^{\cdot} + OsCl_6^- \rightarrow R^+ + OsCl_6^{2-} \qquad (11)$$

However, we now see from the stoichiometry of the R_4Sn reaction [3 equivalents of Os(V) consumed] and fate of the Os complex [$OsCl_6^{2-}$ formed first and then transformed into a second Os(IV) species] that the reaction must be more complex than shown in eqns. (9)–(11) above. The detection of a rearranged product in low yield (2-chlorobutane) from Bu_4Sn is an indication that the reaction at least partially proceeds via a carbocation, but this cannot be the whole story.

The benzyltrimethylsilanes behaved kinetically in the same simple way as the tetraalkylstannanes. Baciocchi et al.[12] observed the same type of kinetics in the reaction between 12-tungstocobaltate(III) ion and a series of benzyltrimethylsilanes and assumed that the mechanism consisted of an initial reversible electron-transfer step, followed by an irreversible, very fast cleavage of the benzyltrimethylsilane radical cation [similarly to eqns. (9) and (10)]. Thus it is reasonable to assume that the $OsCl_6^-/R_4Si$ reaction follows the same mechanism in these steps, supported by the $2:1$ Os(V)/substrate stoichiometry and the clear-cut formation of $OsCl_6^{2-}$. The fate of the benzylic radical is different; in the tungstocobaltate(III) reaction two-electron oxidation products are unambiguously observed, whereas the $OsCl_6^-$ reaction gives benzylic chlorides as the main products. In principle, these might be formed via a radical and/or cationic pathway, but since the product distribution is not affected by the addition of an external nucleophile, such as acetate ion, we assume that the radical pathway is the prevailing one. Chloro complexes are known to act as chlorine-atom donors,[17] so that $OsCl_6^-$ and/or $OsCl_6^{2-}$ must then be assumed to fulfil this role [eqn. (12)]. The fact that two equivalents of Os(V) are

$$R^{\cdot} + OsCl_6^-(OsCl_6^{2-}) \rightarrow RCl + OsCl_5^-(OsCl_5^{2-}) \qquad (12)$$

consumed for each molecule of product formed, means that k_1 is obtained as $k_{obs}/2$.

Table 5 shows a summary of rate constants obtained for $OsCl_6^-$ reaction with organic substrates, together with parameters connected with the Marcus treatment of outer-sphere electron-transfer reactions. The k_1 value for naphthalene needs some comment, since it was previously[2] given as $5.3(5)$ dm^3 mol^{-1} s^{-1} and now as $19(6)$ dm^3 mol^{-1} s^{-1}, an increase by a factor of 3.6. This is due to a mistake in the computational procedure which employed eqn. (8) in inverted form. By plotting $1/P(2)$ against $1/[Nu^-]$ at constant [substrate] the intercept, $1/k_1[\text{substrate}]$, can be calculated and used to estimate k_1, provided the value of the intercept is not too close to zero (a common problem of doubly reciprocal plots). Our regrettable mistake was to plot $1/P(2)$ against $1/[\text{sub-strate}]$ at constant $[NBu^-]$ which cannot give a correct value of k_1, since $1/[\text{substrate}]$ then appears in both terms on the right side of the equation.* The same faulty procedure was used to estimate k_1 for 4-methoxytoluene and here the correct one could not be applied since the intercept turned out to be negative, a recognized problem of doubly reciprocal plots when the intercept is too small. This means that k_1 for 4-methoxytoluene should be larger than the value given previously, and it is presently not possible to estimate by how much.

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* We are indebted to Prof. E. Baciocchi, University of Rome, for spotting this error.

Table 5. Summary of rate constants of $OsCl_6{}^-$ reactions, redox parameters of substrates and effective free energy changes of electron transfer $(\Delta G°')$. Data from Refs. 12 and 18, unless otherwise stated. $E°(Os^V/Os^{VI}) = 1.40$ V vs. NHE, radius of $OsCl_6{}^{-/2-} = 4.1$ Å (Ref. 2).

Substrate	$E°$/V vs. NHE	$\lambda(0)$/ kcal mol^{-1}	Radius/Å	k_1/mol dm^{-3} s^{-1}	$\Delta G°'$/ kcal mol^{-1} [a]
Tetramethylstannane	1.95	52	4.4	10.1	10.4
Tetraethylstannane	1.49	66	5.9	5.7×10^4	-0.1
Tetrapropylstannane	1.52	58	6.5	3.0×10^4	0.9
Tetrabutylstannane	1.52[b]	58[b]	7.0	3.9×10^4	0.9
Benzyltrimethylsilane	2.06	61	4.4	8.1	12.9
Trimethyl(p-tolyl)silane	1.85	61	4.4	4.8×10^2	8.0
4-Fluorobenzyltrimethylsilane	2.05[c]	61	4.4	8.8	12.7
3-Chlorobenzyltrimethylsilane	2.35[c]	61	4.4	0.53	19.6
Naphthalene	2.08	30	2.5	19(6)	12.7

[a] Calculated as $\Delta G° + 331.2 \ (z_1 - z_2 - 1)/(Dr_{12})$, where z_1 is the charge of the oxidant (-1), z_2 is the charge of the substrate (0), D is the relative permittivity of the solvent (taken to be 34[26]) and r_{12} is the distance between the centers of the reactants at collision distance in the transition state. [b] Assumed to be the same as that of tetrapropylstannane. [c] Determined by Dr. E. Fasella, University of Rome.

It should also be noted that the same method was applied to the 4-methoxytoluene/12-tungstoco-baltate(III) data,[2] giving $k_1 = 1.0 \times 10^{-2}$ instead of 1 dm^3 mol^{-1} s^{-1}, calculated in the correct way in a different context.[19] The latter value carried high error limits and a later study by Baciocchi *et al.*[20] under identical conditions gave the k_1 value of ≈ 0.10 dm^3 mol^{-1} s^{-1}. Luckily, for both the naphthalene/$OsCl_6{}^-$ and 4-methoxytoluene reactions the differences between the wrongly and correctly estimated values are small enough for conclusions based on the erroneously computed values to be essentially unchanged.[21]

Comparison with other data. Extensive studies of the reaction between alkylmetals (Si, Sn, Pb and Hg compounds) and iron(III)–phenanthroline complexes solidly established this reaction type as being outer-sphere.[11a,b] These reactions can then be used as the anchor point for the present analysis, in that they define a Marcus plot corresponding to a reorganization energy (λ) of 36 kcal mol^{-1}; in combination with photo-ET oxidation kinetics of a similar set of alkylmetals[22] a λ value of 41 kcal mol^{-1} was obtained.[11c] The solid lines of Fig. 3 correspond to these λ values and are taken to define the region of outer-sphere behaviour of a redox system similar to ours [the differences between the the reorganization energies of the three oxidants are relatively small, being 14,[23] 20–25,[21] and 20 (Ref. 2) kcal mol^{-1}, respectively, for the Fe(III)/(II), Co(III)/(II) and Os(V)/(IV) redox couples discussed here].

A second calibration system is provided by reactions between 12-tungstocobaltate(III) ion and X-benzyl-trimethylsilanes. Baciocchi *et al.*[12] analyzed their 12-tungstocobalt(III)ate/silane reactions by the Marcus theory and obtained reasonable agreement between theory and experiment, provided the reorganization energy of the self-exchange reaction $ArCH_2Si(CH_3)_3{}^{•+}/ArCH_2Si(CH_3)_3$ was accepted to be 61 kcal mol^{-1}. These data (filled circles) are also included in Fig. 3, together
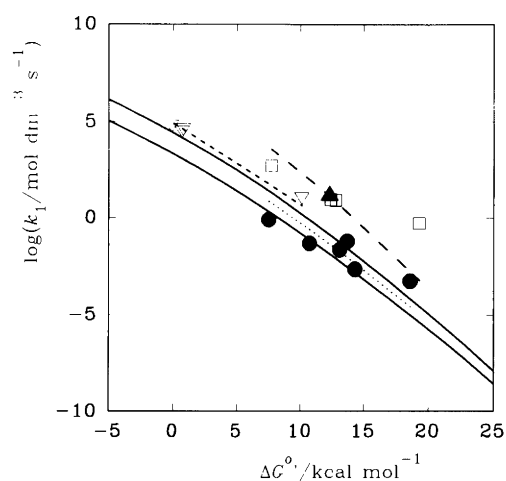
Fig. 3. Marcus plots for $OsCl_6{}^-$/stannanes ($\triangledown$), $OsCl_6{}^-$/ benzyltrimethylsilanes ($\square$) and 12-tungstocobaltate(III)/ benzyltrimethylsilanes ($\bullet$). The solid lines refer to outer-sphere ET reactions between alkylmetals and iron(III)–phenanthrolines [Ref. 11(a), (b); see also text]. The $OsCl_6{}^-$/naphthalene point is marked by $\blacktriangle$.

with the best-fitting Marcus parabola [dotted line; assuming $\log(k_d/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 10$ and the A factor $= 0.1$, which gives the best fit for $\lambda = 39(2)$ kcal mol^{-1}]. This value differs slightly from that derived by Baciocchi *et al.*[12] who obtained $\lambda = 43(6)$ kcal mol^{-1}, using $\log k_d = 10.8$.

Our data on $OsCl_6{}^-$/tetraalkylsilane reactions from Table 5 (squares) are seen to be located slightly above and to the right of the Fe(III)(phen)$_3$/Fe(II)(phen)$_3$ data regression lines and the 12-tungstocobaltate(III) data; one can *formally* fit them to a Marcus parabola (long-dashed line) but the fit is not a good one, as seen on the graph of Fig. 3 and indicated by the large errors in the λ value obtained, 23(7) kcal mol^{-1}. Of course one can argue that this calculation was based on a choice of $E°[Os(V)/Os(IV)]$ in the low part of the possible range

(1.40 V). However, even with $E° = 1.48$ V, no good fit to the Marcus equation was possible. On the other hand, the $OsCl_6^-$/tetraalkylstannane data (Fig. 3, triangles) fit well with outer-sphere behaviour, λ for the best fit to the Marcus equation being 33(2) kcal mol^{-1} (dashed line to the left).

The $OsCl_6^-$/naphthalene point (▲ in Fig. 3) can formally be located on a parabola with $\lambda = 20$ kcal mol^{-1}, with the assumption that $E°(OsCl_6^-/OsCl_6^{2-}) = 1.40$ V, and on one with $\lambda = 27$ kcal mol^{-1} with this potential put at its highest value, 1.48 V. With $\lambda(0)$ of the osmate couple assumed to be 20 kcal mol^{-1}, λ(naphthalene·$^+$/naphthalene) comes out at 20 or 34 kcal mol^{-1}, respectively. As pointed out earlier,[21] this is larger than $\lambda(0)$ values computed from kinetic data on self-exchange reactions of ArH·$^+$/ArH systems (≈ 10 kcal mol^{-1}), pointing to an inner-sphere contribution to the latter due to π complex formation.

The $OsCl_6^-$/tetraalkylsilane data deviate somewhat from the behavior defined by the systems used to calibrate outer-sphere behaviour. The arguments for the outer-sphere nature of the Fe(III)–phenanthroline/alkylmetal reaction are strong and well established,[11] and there is now also good evidence that 12-tungstocobaltate ion/alkylmetal reactions are of the outer-sphere type[12] (Fig. 3). The latter adhere closely to outer-sphere behaviour owing to the chemical inertness of the 12-tungstocobaltate(III) ion.[21,24] It is composed of spherically arranged tungsten oxide segments, exposing only non-basic oxygens toward the solution, and the Co(III) ion is located in the center of the cluster, inaccessible for contact with the substrate. Hexachloroosmate ion seems to deviate from these requirements in some cases; instead an inner-sphere type mechanism might be possible, with a transition state with partial bonding between the complex ion and the silicon atom. A similar but more distinct difference has been found earlier for reactions between alkylmetals (R_4Si, R_4Sn, R_4Pb, R_2Hg) and Fe(III)–phenanthrolines (outer-sphere mechanism) and hexachloroiridate(IV) (inner-sphere mechanism), respectively.[11b]

Experimental

Chemicals. Tetraphenylphosphonium hexachloroosmate was prepared according to the method given by Magnuson.[4] Acetonitrile (UVASOL, Merck) was dried and stored over 3 Å molecular sieves. The substituted benzyltrimethylsilanes were prepared in a Grignard coupling reaction between the X-benzyl chloride and chlorotrimethylsilane.[25] All other chemicals were of the highest quality commercially available.

Analyses. GLC was performed using a Varian 1400 gas. chromatograph equipped with an integrator (HP 3380 A) on a 2 m × 3 mm 5 % NPGS on Chromosorb P column or an HP 5890 Ser. II gas chromatograph equipped with an HP 3396 Ser. II integrator on a 25 m OV-1701 capillary

column. Products were identified by comparison of their GLC retention times and mass spectra with those of authentic specimens (Finnigan 4021 mass spectrometer). NMR spectra were recorded on a Varian XL-300 instrument. Yields and isomer distributions were determined by GLC using toluene as an internal standard, calibrated against authentic samples.

Product studies. The substrate (~ 10 mmol dm^{-3}) was added to a solution of tetraphenylphosphonium hexachloroosmate(V) (5–10 mmol dm^{-3}) in acetonitrile/acetic acid (90/10 v/v) or acetonitrile. The mixture was stirred at ambient temperature until the colour changed to yellow. Work-up consisted of sodium hydrogencarbonate neutralization followed by extraction with diethyl ether and GLC analysis.

Determination of potentials of the substrates. The $E°(R_4Si·^+/R_4Si)$ values were determined by the method employed by Baciocchi et al.[12,27] and kindly performed by Dr. E. Fasella, Department of Chemistry, University of Rome. Anodic peak potentials were measured by cyclic voltammetry in acetonitrile/tetrabutylammonium hexafluorophosphate (0.1 mol dm^{-3}) at a sweep rate of 200 mV s^{-1} (BAS-100 instrument).

Kinetics. Slow kinetic experiments were performed by monitoring the disappearance of hexachloroosmate(V) at 500 nm by a Hewlett-Packard 8452A diode-array spectrophotometer, equipped with an HP 89500 UV–VIS Chemstation. The temperature of the cell was kept at 20.0°C. Moderately rapid reactions were monitored by the same instrument in an RX.1000 stopped-flow accessory available from Applied Photophysics Limited. Fast kinetic measurements were performed with a Hi-Tech SF-3L stopped-flow instrument, equipped with an SF-3C control unit and DSF-3 data display system (from Hi-Tech Scientific Ltd., England). The system was connected to an HP-9835A computer for control of the measurements and calculation of rate constants (Hewlett-Packard NONLIN program).

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