4684 *J. Org. Chem.* 1992, *57*, 4684–4689

A Kinetic Study of the Electron-Transfer-Initiated Carbon–Silicon Bond Cleavage Reactions of Benzyltrialkylsilanes Promoted by 12-Tungstocobalt(III)ate Ion

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Received February 12, 1992

The reactions of some ring-substituted benzyltrimethylsilanes (**1Z**), (*p*-methylbenzyl)triethylsilane (**2**), (*p*-methylbenzyl)triisopropylsilane (**3**), and (*p*-methoxybenzyl)triisopropylsilane (**4**) with potassium 12-tungstocobalt(III)ate, $K_5[Co^{III}W_{12}O_{40}]$ (Co(III)W), have been studied in AcOH–H_2O. In all cases desilylated products, benzyl acetates, and benzyl alcohols have been obtained, with a 2:1 oxidant to substrate stoichiometry. A kinetic investigation has shown that the reactions of **1Z** and **2** are strictly first order in Co(III)W and first order in the substrate. Added salts ($NaClO_4$, NaOAc) decrease the rate, whereas no retarding effect by Co(II)W has been noted. In contrast, the reaction of **4** is no longer first order in Co(III)W and the rate is significantly decreased by added Co(II)W. These data have been interpreted in terms of an electron-transfer mechanism, in which a benzyltrialkylsilane radical cation is formed and then undergoes a C–Si bond cleavage to form a benzyl radical. Reaction of this radical with Co(III)W leads to the products. In the reactions of **1Z** and **2** the rate-determining step is the transfer of the electron from the substrate to Co(III)W, whereas in the reaction of **4** the slow step is the one where the C–Si bond cleavage takes place. The mechanistic changeover is probably related to the much lower rate of C–Si bond cleavage in $\mathbf{4}^{+\bullet}$ than in $\mathbf{1Z}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$, due to the fact that in the former cation radical nucleophilic attack at silicon is made difficult by the bulky isopropyl groups. The kinetic data for the reactions of **1Z** and **2** fit the Marcus equation for a reorganization energy λ of 43 ± 1 kcal mol^{-1}. From this value a λ value of 61 kcal mol^{-1} for the couple $ArCH_2SiMe_3^{+\bullet}/ArCH_2SiMe_3$ has been evaluated, which is somewhat higher than that found for a number of $ArCH_3^{+\bullet}/ArCH_3$ systems. The possible reasons for this difference are discussed on the basis of ab initio calculations (STO-3G) concerning bond distances and angles in $PhCH_3^{+\bullet}$ and $PhCH_2SiH_3^{+\bullet}$.

Benzyltrimethylsilanes have a number of desirable properties for mechanistic studies of electron-transfer oxidations of aromatic systems. First, there is little doubt concerning the operation of an electron-transfer mechanism which is made immediately evident by the nature of the reaction products. Accordingly, benzyltrimethylsilane radical cations undergo a fast C–Si bond cleavage, giving benzyl radicals and the products derived therefrom.[1] Second, since CH_2SiMe_3 is a good electron-donor group, the oxidation potentials of benzyltrimethylsilanes are relatively low; therefore these substrates can react with a large variety of oxidizing systems. An additional advantage is that the oxidation potentials can also be modulated to some extent by appropriate ring substituents. Finally, by changing the alkyl groups bonded to silicon, the rate of C–Si bond cleavage in the radical cation can be varied, without altering the redox properties of the substrates.[1b]

On the side of the oxidizing systems, recent work has suggested that heteropolyanions are very suitable oxidants for quantitative investigations of electron-transfer reactions of organic compounds.[2,3] In view of their characteristic structure (a central ion surrounded by a spherical sheath of chemically inert oxygen atoms[4]), these anions cannot significantly interact with the organic substrates in the transition state of the oxidation process, reacting therefore via an outer-sphere electron-transfer mechanism, which is that more amenable to theoretical treatment.

On the basis of the previous considerations, we have felt that a kinetic study of the oxidation reactions of benzyltrimethylsilanes with an heteropolyanion could provide interesting insight on the general characteristics of a well-behaved outer-sphere electron-transfer process. The merits of this approach would of course be significantly increased if, as it is likely in view of the very fast C–Si bond cleavage in the intermediate radical cation, the reaction rate is determined in the electron-transfer step. This would allow us to get important information on this step directly from the observed rate constants.

In this paper we report on a detailed kinetic study of the reaction of ring-substituted benzyltrimethylsilanes **1Z** (Z = H, *m*-Me, *p*-Me, *m*-OMe, *p*-OMe, *p*-Cl) with potassium 12-tungstocobalt(III)ate, $K_5[Co^{III}W_{12}O_{40}]$ (Co(III)W), in AcOH–H_2O. (*p*-Methylbenzyl)triethylsilane (**2**), (*p*-methylbenzyl)triisopropylsilane (**3**), and (*p*-methoxybenzyl)triisopropylsilane (**4**) have also been investigated in looking for the role of the silicon-bonded alkyl groups.

A thorough kinetic investigation of the oxidation of *p*-methoxytoluene with potassium dodecatungstocobaltate has been reported.[2] Evidence for an electron-transfer step, followed by a rate-determining deprotonation of the radical cation, was obtained.

Results

The reaction of potassium 12-tungstocobalt(III)ate (Co(III)W) with benzyltrialkylsilanes **1Z**, **2**, **3**, and **4** has been studied in a 70:30 AcOH–H_2O mixture, this particular composition of the medium being imposed by solubility problems of either the silanes or Co(III)W. Under these reaction conditions, formation of benzyl alcohols and benzyl acetates has been observed with all substrates investigated. Trialkylsilanols, trialkylsilyl acetates, and siloxanes were also detected among the products. With **3**, the reaction is very sluggish (only 8% in 20 h) and leads to the formation of products of oxidation at the methyl

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Table I. Kinetic Data for the Oxidation of Compounds 1Z and 2 by Co(III)W in AcOH/H_2O (70:30) in a Variety of Conditions

Z	[Co(III)-W], M	[subst], M	[salt], M	k_{obs}, $M^{-1}\ s^{-1}$ [a]
H (55 °C)	2.5×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.1	2.4×10^{-3}
	5.0×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.1	2.3×10^{-3}
	1.0×10^{-3}	1.5×10^{-2}	$NaClO_4$, 0.1	2.4×10^{-3}
	5.0×10^{-4}	1.5×10^{-2}		1.1×10^{-2}
	5.0×10^{-4}	1.5×10^{-2}	NaOAc, 0.1	2.3×10^{-3}
H (25 °C)	5.0×10^{-4}	1.5×10^{-2}		5.6×10^{-4}
m-Me (55 °C)	2.5×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.1	7.8×10^{-3}
	5.0×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.1	7.5×10^{-3}
	1.0×10^{-3}	1.5×10^{-2}	$NaClO_4$, 0.1	8.0×10^{-3}
	4.9×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.1	7.2×10^{-3} [b]
	5.0×10^{-4}	1.5×10^{-2}		3.0×10^{-2}
	2.5×10^{-4}	7.5×10^{-3}		2.9×10^{-2}
m-Me (25 °C)	5.0×10^{-4}	1.5×10^{-2}		2.3×10^{-3}
p-Me (55 °C)	2.5×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.1	1.1×10^{-1}
	5.0×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.1	1.5×10^{-1}
	1.0×10^{-3}	1.5×10^{-2}	$NaClO_4$, 0.1	1.1×10^{-1}
p-Me (45 °C)	5.0×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.1	6.8×10^{-2}
p-Me (35 °C)	5.0×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.1	3.4×10^{-2}
p-Me (25 °C)	5.0×10^{-4}	1.5×10^{-2}		6.2×10^{-2}
	4.5×10^{-4}	1.5×10^{-2}		6.0×10^{-2} [c]
	2.5×10^{-4}	7.2×10^{-3}		6.4×10^{-2}
	5.0×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.021	2.5×10^{-2}
	5.0×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.048	1.9×10^{-2}
	5.0×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.098	1.5×10^{-2}
	5.0×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.18	1.4×10^{-2}
	5.0×10^{-4}	1.5×10^{-2}	NaOAc, 0.1	1.6×10^{-2}
m-MeO (25 °C)	2.5×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.1	1.4×10^{-2}
	5.0×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.1	1.4×10^{-2}
	4.5×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.1	1.4×10^{-2} [b]
	5.0×10^{-4}	1.5×10^{-2}		4.9×10^{-2}
	2.5×10^{-4}	8.4×10^{-3}		4.6×10^{-2}
	5.0×10^{-4}	1.5×10^{-2}	NaOAc, 0.1	2.6×10^{-3}
p-MeO (25 °C)	5.0×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.1	4.6×10^{-1}
	1.0×10^{-3}	1.5×10^{-2}	$NaClO_4$, 0.1	4.5×10^{-1}
	4.9×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.1	4.5×10^{-2}
	5.0×10^{-4}	1.5×10^{-2}		8.0×10^{-1}
	5.0×10^{-4}	1.7×10^{-2}	NaOAc, 0.1	3.5×10^{-1}
2 (55 °C)	2.5×10^{-4}	1.5×10^{-2}	NaOAc, 0.1	1.2×10^{-2}
	5.0×10^{-4}	1.5×10^{-2}	NaOAc, 0.1	1.2×10^{-2}
	2.5×10^{-4}	1.0×10^{-2}	NaOAc, 0.1	1.3×10^{-2}
	5.0×10^{-4}	1.5×10^{-2}		3.1×10^{-1}
	5.0×10^{-4}	1.5×10^{-2}	$NaClO_4$, 0.1	4.8×10^{-2}
2 (25 °C)	5.0×10^{-4}	1.5×10^{-2}		2.3×10^{-2}

[a] The average error is ±5%. [b] In the presence of Co(II)W 4.9×10^{-2} M. [c] In the presence of Co(II)W 4.5×10^{-2} M.

Table II. Kinetic Data for the Oxidation of 4 by Co(III)W in AcOH/H_2O (70:30) at 55 °C

[substr], M	[Co(III)W], M	[salt], M	k, s^{-1}
1.5×10^{-2}	2.6×10^{-4}	NaOAc, 0.1	3.2×10^{-3}
1.5×10^{-2}	2.6×10^{-4}	NaOAc, 0.1	1.6×10^{-3} [a]
1.7×10^{-2}	5.1×10^{-4}	NaOAc, 0.1	2.2×10^{-3}
1.5×10^{-2}	5.1×10^{-4}		8.7×10^{-3}
1.5×10^{-2}	2.6×10^{-4}		1.1×10^{-2}
1.5×10^{-2}	2.5×10^{-4}	$NaClO_4$, 0.1	1.1×10^{-2}
1.5×10^{-2}	2.5×10^{-4}	$NaClO_4$, 0.1	6.0×10^{-3} [b]
1.5×10^{-2}	5.0×10^{-4}	$NaClO_4$, 0.1	8.0×10^{-3}
1.5×10^{-2}	9.7×10^{-4}	$NaClO_4$, 0.1	4.7×10^{-3}

[a] In the presence of Co(II)W 2.6×10^{-4} M. [b] In the presence of Co(II)W 2.5×10^{-4} M.

group together with the expected desilylation products. No kinetic study was therefore carried out with this compound or with **1** (Z = *p*-Cl), which also exhibited a low reactivity.

The stoichiometry of the reaction, which has been checked with compounds **1** (Z = H) and **1** (Z = *p*-CH_3) is reported in eq 1 (X = OH, OAc).

$$ArCH_2SiMe_3 + 2\ Co(III)W^{5-} \xrightarrow{AcOH/H_2O} ArCH_2X + 2\ Co(II)W^{6-} + Me_3SiX \quad (1)$$

For compounds **1Z**, **2** and **4** reaction rates have been investigated, at either 25 or 55 °C (depending on the substrate reactivity) by following the disappearance of Co(III)W spectrophotometrically at 390 nm. An excess of silane (at least 20 times) was always used, whereas the Co(III)W concentration ranged from 2.5×10^{-4} to 10^{-3} M. With all substrates, except **4**, excellent first-order plots were obtained up to 90–95% of reaction. From the first-order rate constants the second-order rate constants (k_{obs}) were calculated as usual and found to be independent of both Co(III)W and substrate concentration. No rate-retarding effect by Co(II)W was observed, whereas a decrease in k_{obs} was found when the reaction was carried out in the presence of salts (either $NaClO_4$ or AcONa). All data are reported in Table I.

Clearly, these observations indicate that the process described in eq 1 follows clean second-order kinetics, being first order in the substrate and first order in Co(III)W, this conclusion holding also for the reaction of the triethylsilane **2**. The influence of the temperature has been determined for the reaction of **1** (Z = *p*-CH_3) in the interval between 25 and 55° C (Table I). An excellent ($r = 0.9999$) log k_{obs} vs $1/T$ plot was obtained from which the activation parameters ($\Delta H^* = 14.7$ kcal mol^{-1}, $\Delta S^* = -19.7$ cal K^{-1} mol^{-1}) were obtained.

A different kinetic situation holds for the oxidation of compound **4**. In this case deviations from first-order plots were observed and, more importantly, the first-order rate constants, evaluated from the first portion of the plot, were not independent of the initial concentration of Co(III)W but were observed to decrease as [Co(III)W] increased. Moreover, a decrease in the reaction rate was observed in the presence of Co(II)W. In this case too, the oxidation rate decreased in the presence of salts. These results are displayed in Table II.

For quantitative treatment of the kinetic data in terms of the Marcus equation we also needed the values of the standard oxidation potentials ($E°$) of the benzyltrimethylsilanes investigated. The direct measurement of these values is, however, very difficult in view of the high fragmentation rate of the formed radical cation, which makes the cyclic voltammogram irreversible. This situation is common in studies of electron-transfer reactions, especially in those of alkylmetals,[5] and it has made necessary the use of indirect approaches to estimate the $E°$ values.[7] In our case we have circumvented this problem by exploiting the existence of a good linear relationship between the $E°$ values of a series of methyl- and alkylbenzenes in CH_3CN and the $h\nu_{ct}$ values of the charge transfer (CT) complexes of these compounds with tetracyanoethylene.[8] This relationship is described by eq 2, where the values of $E°$ are in volts (vs NHE) and those of $h\nu_{ct}$ are in electron-volts.

$$E°(V) = 0.862 h\nu_{ct} - 0.131 \quad (2)$$

By reasonably assuming that benzylsilanes also follow the same relationship, we have measured the $h\nu_{ct}$ values of the absorption bands of their charge-transfer complexes with tetracyanoethylene and calculated the $E°$ values using eq 2. These data are in Table III.

Discussion

We have already mentioned that the cleavage of the C–Si bond is the distinctive fate of benzyltrimethylsilane radical cation. Therefore, the observation that Co(III)W induces a clean desilylation reaction leading to benzyl

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Table III. $h\nu_{ct}$ and Calculated $E°$ Values for Some Benzyltrialkylsilanes

compd	$h\nu_{ct}$,[a] eV	$E°$,[b] V
1 (Z = H)	2.55	2.06
1 (Z = *m*-Me)	2.33	1.88
1 (Z = *p*-Me)	2.30	1.85
1 (Z = *m*-MeO)	2.15	1.72
1 (Z = *p*-MeO)	1.99	1.58
2	2.27	1.82
4	1.97	1.57

[a] Determined from the absorption maximum of the longer wavelength band of the charge-transfer complex between the benzylsilanes and tetracyanoethylene in CH_2Cl_2. [b] vs NHE. Calculated using eq 2.

derivatives, with all compounds **1Z**, as well as with **2** and **4**, is by itself a clear indication that an electron-transfer mechanism is operating. Very likely, the reactions of these compounds can be described by the mechanistic sequence reported in eqs 3–6 (X = OH, OAc). The radical cation,

$$ArCH_2SiMe_3 + Co(III)W^{5-} \underset{k_{-el}}{\overset{k_{el}}{\rightleftharpoons}} ArCH_2SiMe_3^{+\bullet} + Co(II)W^{6-} \quad (3)$$

$$ArCH_2SiMe_3^{+\bullet} + HX \xrightarrow{k_2} ArCH_2^{\bullet} + Me_3SiX + H^+ \quad (4)$$

$$ArCH_2^{\bullet} + Co(III)W^{5-} \rightarrow ArCH_2^+ + Co(II)W^{6-} \quad (5)$$

$$ArCH_2^+ + HX \rightarrow ArCH_2X + H^+ \quad (6)$$

formed in the first step, is desilylated, with the nucleophilic assistance of the solvent,[1b] to give the benzyl radical which is oxidized by another Co(III)W ion and converted into products.

The finding that all trimethylsilyl derivatives **1Z** as well as the triethylsilane **2** react by kinetics which are cleanly first order in Co(III)W, without any evidence for a rate-retarding effect by Co(II)W, strongly indicates that the electron-transfer step (eq 3) is the one determining the reaction rate. Thus, for the reactions of **1Z** and **2** the observed second-order rate constants, k_{obs}, reported in Tables I–IV, should coincide with the rate constants k_{el} for the step where the electron is transferred from the substrate to Co(III)W.

This conclusion is also supported by the lack of any rate-enhancing effect of AcONa. If the nucleophile-assisted C–Si bond cleavage would contribute to the overall oxidation rate, we would expect a faster rate in the presence of AcONa, since AcONa should be a stronger nucleophile toward silicon than either AcOH or H_2O. In fact, as shown in Table I, AcONa decreases the rate as $NaClO_4$ does, thus indicating that it only exerts a ionic strength effect (see infra).

If the above conclusions are correct, it appears that benzylsilanes behave quite differently than 4-methoxytoluene with respect to the electron-transfer reaction with Co(III)W. Accordingly, as already mentioned, in the reaction of the latter substrate the electron-transfer step occurs in a preequilibrium and the slow step is the proton loss from the intermediate radical cation. This difference, however, can easily be rationalized by considering that deprotonation of an alkylaromatic radical cation has been found to be a much slower process than desilylation of a benzyltrimethylsilane radical cation.[9]

The discussion of the kinetic data for **1Z** and **2** in terms of the Marcus theory[6,10] appears appropriate since, as already stated, Co(III)W should react by an outer-sphere electron-transfer mechanism. In the Marcus theory (Scheme I) an electron donor D and an electron acceptor A are suggested to first diffuse together, giving an encounter complex which then undergoes an electron-transfer reaction to form a geminate radical ion pair eventually leading to the products. The activation free energy (ΔG^*) and the standard free energy change of the electron-transfer step, corrected for the electrostatic interactions arising from the variation of charge in A and D upon electron transfer, $\Delta G°'$, are correlated by the Marcus equation, which, when a neutral organic molecule is involved, has the form of eq 7, where λ is the reorganization

Scheme I

$$D + A \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} (D\ A) \underset{k_{-el}}{\overset{k_{el}}{\rightleftharpoons}} (D^{+\bullet} A^{-\bullet}) \xrightarrow{k_s} D^{+\bullet} + A^{-\bullet}$$

Table IV. Values of $\Delta G°$, $\Delta G°'$, and k_{obs} for the Reactions of 1Z and 2 with Co(III)W in AcOH/H_2O (70:30) at 25 °C

compd	$\Delta G°$ [a]	$\Delta G°'$ [b]	k_{obs},[c] M^{-1} s^{-1}
1 (Z = H)	24.3	18.6	5.6×10^{-4}
1 (Z = *m*-Me)	20.0	14.3	2.3×10^{-3}
1 (Z = *p*-Me)	19.4	13.7	6.2×10^{-2}
1 (Z = *m*-MeO)	16.4	10.7	4.9×10^{-2}
1 (Z = *p*-MeO)	13.2	7.5	8.0×10^{-1}
2	18.8	13.1	2.3×10^{-2}

[a] Calculated using eq 9. [b] Calculated by eq 10. [c] From Table I. Data obtained in the absence of added salts.

$$\Delta G^* = \lambda/4 \times [1 + \Delta G°'/\lambda]^2 \quad (7)$$

energy representing the energy associated with adjustments in the nuclear geometries and solvent shells of the interacting species which are required to make possible the transfer of the electron from the donor to the acceptor.[6] Since k_{el}, the rate constant for the electron-transfer step, is given by $Ze^{-\Delta G^*/RT}$ and Z can be taken as 6×10^{11}, from eq 7 we obtain eq 8, which directly relates the rate constants to the $\Delta G°'$ value. The latter are calculated from

$$\log k_{obs} = 11.78 - (\lambda/9.2RT)(1 + \Delta G°'/\lambda)^2 \quad (8)$$

the $\Delta G°$ values (expressed in kcal mol^{-1}) obtained by eq 9, using the $E°$ values determined by eq 2 for the aromatic compounds and the value of 1.01 V vs NHE for Co(III)W.[2]

$$\Delta G° = 23.06[E° - E°_{CoIII/CoII}] \quad (9)$$

The $\Delta G°$ values have then been corrected for the electrostatic interaction on the basis of eq 10, which also takes into account the role of the ionic strength, to give the $\Delta G°'$ value to introduce in the Marcus equation.[6]

$$\Delta G°' = \Delta G° + \{(z_1 - z_2 - 1) \times e^2 \times 10^{-[21.9r_{12}(\mu/DT)^{1/2}]}\}/(D \times r_{12}) \quad (10)$$

In eq 10, e is the electron charge, z_1 and z_2 are the charge numbers of the oxidant (−5) and of the substrate (0), r_{12} is the distance between Co(III)W and the substrate in the encounter complex (taken as 7 Å), μ is the ionic strength (0.0075 μ, in the absence of salts, vide infra), D is the dielectric constant of the solvent (37.4 for the 70:30 AcOH–H_2O mixture), and T is the absolute temperature. The values of $\Delta G°$ and $\Delta G°'$ evaluated as described above are listed in Table IV together with the k_{obs} values which have been used in the Marcus correlation. These values refer to reactions carried out at 25 °C, in the absence of added salts.

In Figure 1, the result is shown of a nonlinear least-squares curve fitting of the experimental data (Table IV),

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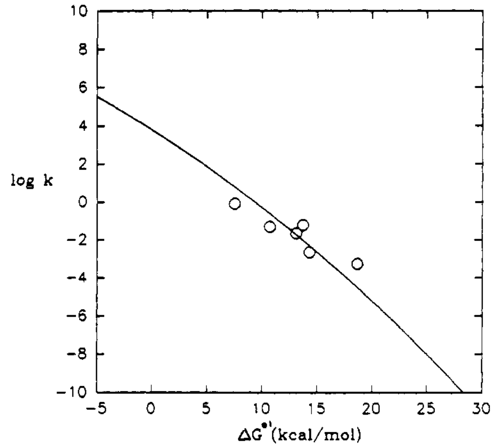

Figure 1. Marcus plot for the reactions of Co(III)W with benzyltrialkylsilanes. The points are the experimental data and the curve has been calculated using eq 8, with a λ value of 43.

to eq 8, using the reorganization energy λ as adjustable parameter. The best fit of the experimental data with the curve calculated by eq 8 is obtained for a λ value of 43 kcal mol^{-1} (standard deviation= 1 kcal mol^{-1}) which represents the overall (reactants and solvent) reorganization energy associated with the transfer of one electron from $ArCH_2SiMe_3$ to Co(III)W under our reaction conditions. The fit is quite satisfactory, especially considering the errors involved in the evaluation of $\Delta G^{\circ\prime}$ values.

The observed negative salt effects are also consistent with predictions by the Marcus equation. Accordingly, eq 10 shows that an increase in the ionic strength causes an increase in the $\Delta G^{\circ\prime}$ value and consequently (eq 7) a decrease in the rate constant for the electron-transfer step. This agreement is however only qualitative since the effects of the ionic strength, calculated by eqs 8 and 10 for the reaction of 1 (Z = p-Me)[11] are larger than the observed ones, the discrepancy increasing as the ionic strength increases. This phenomenon has already been observed in other electron-transfer processes[12,13] and attributed to the fact that eq 10 overcorrects for ionic strength effects outside the Debye–Hückel limiting region.[14]

In the Marcus theory, the reorganization energy for the transfer of one electron from a donor to an acceptor is approximately given by the arithmetic average of the reorganization energies of the donor and acceptor self-exchange reactions, as shown in eq 11. In our case, using

$$\lambda_{AD} = (\lambda_{A/A^{-\cdot}} + \lambda_{D^{+\cdot}/D})/2 \qquad (11)$$

the value of 43 kcal mol^{-1} calculated above and assuming

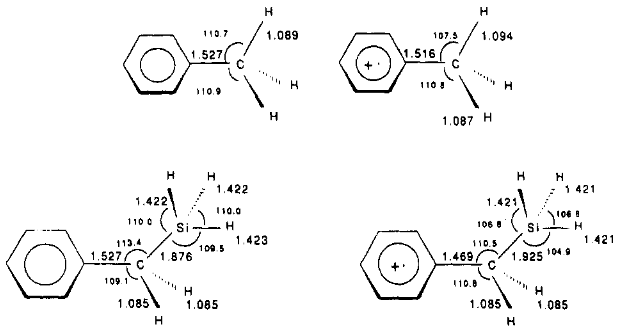

Figure 2. Bond lengths (angstroms) and bond angles (degrees) in toluene, benzylsilane, and their corresponding radical cations obtained by ab initio calculations (STO-3G basis set).

a value of 25 kcal mol^{-1} for the reorganization energy associated with the Co(III)W/Co(II)W couple,[3] it is possible to calculate a value of 61 kcal mol^{-1} for the reorganization energy of the $ArCH_2SiMe_3^{+\cdot}/ArCH_2SiMe_3$ couple. This value is smaller than that evaluated (70 kcal mol^{-1}) for the $SiEt_4^{+\cdot}/SiEt_4$ self-exchange reaction.[15] A very plausible reason is that in the latter system the electron is removed from a carbon silicon σ orbital, with structural modifications which should be, therefore, much more important with respect to those taking place when the electron is removed from an aromatic π system.

Very interestingly, the λ value for the $ArCH_2SiMe_3^{+\cdot}/ArCH_2SiMe_3$ couple seems somewhat larger than the λ values recently calculated for a number of $ArCH_3^{+\cdot}/ArCH_3$ systems, which fall in the 40–55 kcal mol^{-1} range.[3] Thus, it would appear that the replacement of a hydrogen atom by a trimethylsilyl group in the α-carbon of a benzene side chain has some influence with respect to the reorganization energy associated to the loss of one electron from the aromatic system.

The relatively high $\lambda(ArCH_3^{+\cdot}/ArCH_3)$ values, with respect to those of unsubstituted aromatics (ca. 10 kcal mol^{-1}),[16] have reasonably been explained on the basis of the strong hyperconjugative effect of the CH_3 group in the radical cation, which should lead to a substantial reorganization of C–H bond electrons.[17] One would therefore expect a larger λ value for the $ArCH_2SiMe_3^{+\cdot}/ArCH_2SiMe_3$ couple because the σ–π conjugation of a β C–Si bond is much more effective than that of a β C–H bond.[18] Indeed, the E_p value of benzyltrimethylsilane is ca. 0.5 V lower than that of toluene.[19] The hyperconjugative effects of C_α–H and C_α–Si bonds are also supported by ESR measurements for alkylaromatics and benzyltrimethylsilanes radical cations, which indicates the ability of these bonds, especially the C–Si bond, to carry a considerable amount of spin density.[21,22]

However, results of ab initio calculations (STO-3G basis set) do not fit in with this picture, as they indicate only very slight changes in bond angles and bond lengths of benzylsilane and toluene radical cations with respect to the corresponding values in the neutral substrates (Figure 2).[23] This is a very intriguing result since, on this basis,

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[11] We thank a referee for this suggestion.

[12] Halpern, J.; Legare, R. J.; Lumry, R. *J. Am. Chem. Soc.* **1963**, *85*, 680.

[13] Haim, A.; Sutin, N. *Inorg. Chem.* **1976**, *15*, 476.

[14] To deal with this overcorrection, an "averaged" method of evaluating the ionic strength effect has been proposed.[13] In this method, the effect of the ionic strength is calculated at μ = 0 and at the μ used, and the average between these two values is taken. Actually, when the "averaged" method has been used to calculate $\Delta G^{\circ\prime}$ values from eq 10, for the reactions of 1 (Z = p-Me), a very good agreement between the calculated and the observed ionic strength effects on the rate has been found. However, we do think it appropriate not to put too much emphasis on this agreement, since it might be fortuitous in view of the arbitrary nature of the "averaged method". On the other hand, by putting in eq 8 the $\Delta G^{\circ\prime}$ values obtained by the "averaged" method, a λ value of 46 ± 2 kcal mol^{-1} has been calculated, which is very close to that (43 ± 1) evaluated, as described in the text, using the kinetic data and $\Delta G^{\circ\prime}$ values reported in Table IV. This means that changes in $\Delta G^{\circ\prime}$ induced by changes in the ionic strength (or the way ionic strength effects are calculated) are not so relevant as to induce significant changes in the λ values.

[15] Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79, Table 13.

[16] Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer Verlag: Berlin Heidelberg, 1986; Chapter IV.

[17] Eberson, L.; Jóhnsson, L. *Acta Chem. Scand.* **1986**, *B40*, 79.

[18] Pitt, C. G. *J. Organomet. Chem.* **1973**, *61*, 49.

[19] The E_p value of toluene is 2.63 V vs NHE,[20] which compares with the value of 2.1 V for benzyltrimethylsilane (Table IV).

[20] Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 7240.

[21] (a) Rao, D. N. R.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1985**, 991. (b) Rao, D. N. R.; Chandra, H.; Symons, M. C. R. *Ibid.* **1984**, 1201.

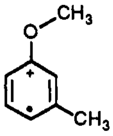
[22] Bock, H.; Kaim, W. *Acc. Chem. Res.* **1982**, *15*, 9.

we would not expect substantial differences between the two systems, with respect to the reorganization energies of self-exchange reactions.

Certainly, the problem of the factors which determine the reorganization energy in the formation of alkylaromatic radical cations appears more complex than predicted and further study is necessary. Probably an important role in this respect might also be played by the solvent. Interestingly, the largest λ value for the $ArCH_3^{+\bullet}/ArCH_3$ couples studied so far (55 kcal mol^{-1}, not far from that determined by us for the $ArCH_2SiMe_3^{+\bullet}/ArCH_2SiMe_3$ couple) has been obtained in a solvent ($AcOH/H_2O$ = 55/45) very similar to that used in the present work. On the other hand, a substantial solvent reorganization is consistent with the negative value of ΔS^* (−19.7 cal K^{-1} mol^{-1}) which has been measured.

Another point of interest is the clean desilylation reaction observed with the (*m*-methoxybenzyl)trimethylsilane (**1Z** = *m*-OCH_3), showing that C–Si bond cleavage in **1Z** (*m*-OCH_3) cation radical has to be a relatively fast process. This finding contrasts with the extremely low deprotonation rate of *m*-methylanisole cation radical, which makes electron-transfer reactants unsuitable for accomplishing the side-chain functionalization of *m*-methylanisole.[26]

In line with the recent discussion by Arnold and coworkers,[27] it can be suggested that, owing to the much greater electron-donating properties of the methoxy group with respect to the methyl group, in *m*-methylanisole cation radical, structure 1 is much more important than structure 2. Consequently very little spin density is placed in the methyl group bearing carbon, which makes very low the reactivity of this group toward the nucleophiles. In contrast, for **1Z** (*m*-OMe)$^{+\bullet}$ structures 3 and 4 may have comparable importance since the electron-donating properties of CH_2SiMe_3 are not much different from those of OCH_3.[28] Thus, in the latter radical cation considerable spin density can reside on the ring carbon bearing the CH_2SiMe_3 group and the nucleophilic attack at the silicon atom of this group becomes feasible.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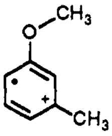
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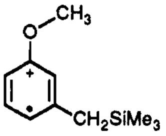
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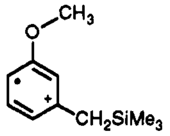
4

We have already noted that the reaction of the triisopropyl derivative **4** behaves differently than those of the substrates we have just discussed. Namely, the reaction is not first order in Co(III)W and, more importantly, it exhibits a significant rate-retarding effect by Co(II)W. Evidently, the cleavage of the C–Si bond is now playing a significant role with respect to the reaction rate. This mechanistic change is not surprising since existing information[1b] clearly indicates that in a benzyltriisopropylsilane radical cation the rate of C–Si bond breaking is several orders of magnitude slower than that in the case of the corresponding trimethylsilyl or triethylsilyl derivatives, probably due to steric hindrance to nucleophilic attack on silicon. Thus, it is certainly plausible that, in going from **1Z** and **2** to **4**, there is such a decrease in the rate of the desilylation step (k_2) so as to make this rate smaller than or at least comparable with k_{-el}[Co(II)W]. It follows that the electron-transfer step becomes reversible and the slow step is the one involving C–Si bond cleavage. Very likely, this situation also holds for compound **3**, whose reactivity indeed was found to be much lower than that of **1** (Z = CH_3). Moreover, with the former compound, but not with the latter, deprotonation at the CH_3 group competes with C–Si bond cleavage (see Experimental Section), thus confirming that the rate of this cleavage is strongly depressed in the derivative with the triisopropylsilyl group.

The observation that the rate of oxidation of **4** is not enhanced by added AcONa contrasts with the previous conclusion since, as already mentioned, AcONa should be a stronger nucleophile toward silicon than either AcOH or H_2O. However, due to steric factors nucleophilic assistance to the cleavage of the C–Si bond in $4^{+\bullet}$ might be much less important than in the corresponding reactions of $1Z^{+\bullet}$ and $2^{+\bullet}$. In this situation differences in the reactivity toward silicon of AcONa, on the one side, and of AcOH and H_2O, on the other side, might not play a significant role with respect to the desilylation rate.

The kinetic data for **4** can be mathematically treated[2] on the basis of the mechanistic scheme involving an electron-transfer preequilibrium followed by a rate-determining C–Si bond cleavage (eqs 3 and 4). This allows us to obtain a value of 1.3 × 10^{-4} s^{-1} for the $(k_{el}/k_{-el})k_2$ parameter. The (k_{el}/k_{-el}) is the equilibrium constant for the electron-transfer step which, from the $E°$ values for Co(III)W and **4**, turns out to be 2.5 × 10^{-9}. Thus a rate constant k_2 of 4 × 10^4 s^{-1} is obtained for the C–Si bond cleavage in $4^{+\bullet}$ in the presence of sodium perchlorate. Dinnocenzo et al.[1b] have reported that in CH_3CN C–Si bond cleavage in $4^{+\bullet}$ occurs at a rate <4 × 10^3 s^{-1}. However, a higher value in $AcOH/H_2O$ is plausible since silicon affinity for an oxygen nucleophile is much higher than that for a nitrogen nucleophile.[30]

Experimental Section

GLC analyses were performed on a Varian 3400 GC using a 25-m × 0.2-mm silica capillary column coated with methylsilicone gum and on a Varian Vista 6000 GC using a 12-m × 0.2-mm fused silica CP Sil OV 17 capillary column.

GC-MS analyses were performed on a HP 5890 GC equipped with a 12-m × 0.2-mm silica capillary column coated with methylsilicone gum and coupled with a HP 5970 MSD.

^1H NMR spectra were recorded on a Bruker WP 80 SY spectrometer.

UV/vis spectra were recorded on a Cary 219, a Varian 634, and a HP 8452 spectrophotometer.

Materials. High purity commercial samples of cobaltous acetate tetrahydrate, sodium tungstate dihydrate, potassium acetate, potassium persulfate, trimethylchlorosilane, triisopropylchlorosilane, triethylchlorosilane, benzyltrimethylsilane, *p*-methoxybenzyl chloride, *m*-methoxybenzyl chloride, *m*-methylbenzyl chloride, *p*-methylbenzyl chloride, magnesium, and methyl benzoate were used as received. Benzyltrimethylsilane required further purification and was distilled under reduced pressure (p.e. 75 °C at 20 mmHg).

Potassium 12-tungstocobalt(III)ate was prepared using the procedure used by Eberson[2] with some modifications. The synthesis starts with the preparation of sodium tungstodicobalt(II)ate from cobaltous acetate and sodium tungstate. The sodium salt is then converted into the potassium salt by treatment with

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[23] Recent calculations[24,25] have indicated that the formation of arylalkane radical cations is not accompanied by changes in the C_α–C bond.

[24] Takahashi, O.; Kikuchi, O. *Tetrahedron Lett.* **1991**, *37*, 4933.

[25] Camaioni, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 9475.

[26] Baciocchi, E.; Rol, C.; Sebastiani, G. V. *Gazz. Chim. Ital.* **1982**, *112*, 513.

[27] Arnold, D. R.; Du, X.; Henseleit, K. M. *Can. J. Chem.* **1991**, *69*, 839.

[28] The σ_p^+ values are −0.31 (CH_3), −0.66 (CH_2SiMe_3), and −0.78 (OMe).[29]

[29] Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds; Plenum Press: New York-London, 1978: Chapter 10.

[30] The bond energies of Me_3Si–OH and Me_3Si–NHMe are 128 and 100 kcal mol^{-1}, respectively (Mc Nillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493).

potassium acetate. Finally the Co(II) complex is oxidized to the Co(III) complex by potassium persulfate. The oxidizing properties have been determined by iodometric titration and correspond to a 98% pure complex, with an extinction coefficient of 1207 at 390 nm (lit.[31] $\epsilon = 1225$ at 390 nm).

Ring-substituted benzyltrimethylsilanes **1Z** (Z = *m*-Me, *p*-Me, *m*-OMe, *p*-OMe), (*p*-methylbenzyl)triethylsilane (**2**), (*p*-methylbenzyl)triisopropylsilane (**3**), and (*p*-methoxybenzyl)triisopropylsilane (**4**) have been prepared by Grignard reaction of the appropriate benzylmagnesium chloride with trialkylchlorosilane in anhydrous THF as described.[32] The products were purified by distillation and/or chromatography on a silica gel column (eluent: petroleum ether 40–70).

Products Analysis. The reactions of **1Z**, **2**, and **4** with Co(III)W in AcOH/H_2O (70:30) lead to a mixture of the corresponding benzyl alcohol and benzyl acetate (comparison with authentic specimen) accompanied by trialkylsilanols, trialkylsilyl acetates, and siloxanes which were recognized by GC-MS analysis. With **3** the reaction was very sluggish and in addition to the above products small amounts of [*p*-(acetoxymethyl)benzyl]triisopropylsilane were observed. The stoichiometry of the process was determined for the reactions of 1 (Z = *p*-CH_3) and 1 (Z = H) as follows. An acetic acid/water (7/3) solution (25 mL) 0.4 M in potassium acetate, 0.032 M in benzyltrimethylsilane, and 0.016 M in K_5Co(III)W was kept at 55 °C for 10 half-lives under an inert atmosphere of argon. Workup was performed according to a procedure described by Eberson[2] and the residue was subjected to GLC and/or ^{1}H NMR analysis (internal standard methyl benzoate). For the reaction of 1 (Z = *p*-CH_3) it was found by GLC analysis that 8.3×10^{-4} mol of substrate and 4.0×10^{-4} mol of Co(III)W gave 2.1×10^{-4} mol of products (1.5×10^{-4} mol of *p*-methylbenzyl alcohol and 0.6×10^{-4} mol of *p*-methylbenzyl acetate). A very similar result was obtained when product analysis was carried out by ^{1}H NMR. In a duplicate experiment 7.9×10^{-4} mol of substrate and 4.0×10^{-4} mol of Co(III)W gave 2.0×10^{-4} mol of product (1.5×10^{-4} mol of alcohol and 0.5×10^{-4} mol of acetate). For the reaction of 1 (Z = H) it was found by ^{1}H NMR analysis that 8.0×10^{-4} mol of substrate reacted with 4.0×10^{-4} mol of Co(III)W to give 2.1×10^{-4} mol of products (1.5×10^{-4} mol of benzyl alcohol and 0.6×10^{-4} mol of benzyl acetate). In a duplicate experiment 8.0×10^{-4} mol of substrate and 4.0×10^{-4} mol of Co(III)W gave 2.0×10^{-4} mol of product (1.6×10^{-4} mol of alcohol and 0.4×10^{-4} mol of acetate). No quantitative determination of the silicon-containing species was carried out.

Kinetic Studies. Acetic acid and water were thoroughly purged with pure argon. A cuvette, containing the solution of benzylsilane (1.5×10^{-2} M) in AcOH/H_2O (70/30), was placed in a thermostated compartment of a UV/vis spectrophotometer. After thermal equilibration the reaction was started by rapid addition (50 to 200 μL) of the K_5Co(III)W solution (1.5×10^{-2} M). The absorbance at 390 nm (A_t) was recorded as a function of time up to when a constant value was reached (A_{inf}). First-order rate constants were obtained from the plot of log $(A_t - A_{inf})/(A_0 - A_{inf})$ against time. A_0 is the initial absorbance value. The effect of Co(II)W was determined by first running a reaction to completeness, thus producing a mixture containing an amount of Co(II)W corresponding to the one of the used Co(III)W. To this mixture Co(III)W was added and the decrease in absorbance with time was recorded.

Charge-Transfer Complexes. The spectra of the charge-transfer complexes of TCNE with benzylsilanes in CH_2Cl_2 were recorded on an HP Vectra spectrophotometer at 25 °C. The spectrum of the solvent was first recorded between 310 and 820 nm. Next the absorbance spectra of a 5×10^{-3} M solution of TCNE (1) and of a 5×10^{-2} M solution of benzylsilane (2) were recorded. Finally the spectrum of a solution (3) containing TCNE and benzylsilane at the same concentration as those above was recorded. Spectra 1 and 2 were subtracted from spectrum 3 to obtain the spectrum of the charge-transfer complex. For compounds 1 (Z = H) and the para-substituted benzyltrialkylsilanes two well-separated CT bands were observed. With 1 (Z = *m*-OMe) and 1 (Z = *m*-Me) the separation of the two CT bands was much less evident, as expected,[33] and it was necessary to carry out the deconvolution of the spectrum. In all cases the values of $h\nu_{ct}$ reported in Table IV were calculated from the λ_{max} values corresponding to the longer wavelength CT band.

Computational Methods. Ab initio theoretical calculations were carried out by using GAUSSIAN 88[34] with the standard STO-3G basis set on an IBM 3090/600J computer (CICS, Università "La Sapienza", Roma). RHF and UHF geometries were obtained respectively for neutral and radical cations substrates. In UHF calculations, care was taken to check initial guess for the proper symmetry of the single occupied molecular orbital.[18b] The errors in the bond lengths should not exceed 0.04 Å; those in bond angles should be ca. 3–4°.[35]

Acknowledgment. Thanks are due to the ministry of the University and of Technological Research (MURST) for financial support. We are also grateful to Prof. L. Eberson (University of Lund) for providing us with a manuscript before publication and to Dr. F. Grandinetti (CNR, Montelibretti) for the assistance in quantum mechanical calculations.

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