# Electron Transfer Reactions in Organic Chemistry. VIII* Synchronous Electron-proton Transfer in the Oxidation of Alkylbenzenes by 12-Molybdocerate(IV) Ion**

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A kinetic study of the oxidation of difficultly oxidizable alkylaromatic hydrocarbons (with $E^\circ > 2.2$ V *vs.* NHE) by the heteropoly ion 12-molybdocer(IV)ate [Ce(IV) $Mo_{12}O_{42}^{8-}$, $E^\circ = 1.42$ V; abbreviated Ce(IV)Mo] in acetic acid/water (50/50) at 50 °C has been performed. For a model substrate, *p*-xylene, the rate of disappearance of the cerium(IV) species is first order in each of [Ce(IV)Mo] and [$ArCH_3$] and independent of [$AcO^-$] and Ce(III)Mo. A strong rate retardation is seen in the presence of tetrabutylammonium ion (reaction order $\approx -1$). The products of *p*-xylene oxidation are the expected ones for an electron transfer mediated process under the prevailing reaction conditions, 4-methylbenzyl acetate and 4-methylbenzyl alcohol.

The mechanism is discussed in the context of the Marcus theory. It is concluded that complications due to back electron transfer within the successor complex competing with its dissociation into free ions are serious enough to exclude a rate-determining non-bonded electron transfer step. Instead, the mechanism is probably best described as a synchronous electron-proton transfer reaction.

Heteropoly ions, consisting of a central, oxidizing metal ion and a surrounding shell of tungsten or molybdenum octahedra,[1] are useful mechanistic tools for studying the electron transfer (ET) mediated oxidation of organic molecules. The metal ion is deeply buried inside the shell (Fig. 1 ) and is thus unavailable for bonding toward the substrate. Only oxygens of very low basicity are exposed to the solution, and provided water is present in the medium to occupy any uncoordinated centers on the shell,[2] all chemical reactivity except ability to accept an electron should be minimal. It is an appropriate analogy to denote such an ion a "soluble anode".[3]

12-Tungstocobalt(III)ate ion, with an $E^\circ$ of 1.00 V *vs.* NHE[4] (normal hydrogen electrode; all potentials in the following will be referred to this electrode), was recently[5] shown to oxidize 4-methoxytoluene ($E^\circ = 1.82$ V) in $HOAc/H_2O$

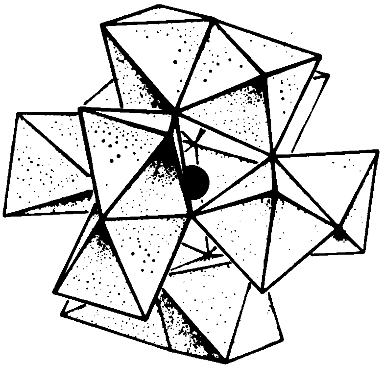

*Fig. 1.* The Ce(IV)$Mo_{12}O_{42}^{8-}$ ion.

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*Part VII. Eberson, L., Jönsson, L., and Sänneskog, O. *Acta Chem. Scand. B 39* (1985) 113.

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(55/45 w./w.) according to an ECE type mechanism [eqns. (1)–(3); $M^+/M$ symbolizes a general $1e^-$ redox reagent]. In this case the $k_2$ step, abstraction of an α proton from the radical cation, was the rate-determining one. As evidence for this conclusion was cited first-order dependence upon [$ArCH_3$] and [B:] (added as acetate ion) at low base concentrations, inverse first-order dependence upon $[M]_0$ and a high $k_H/k_D$ (6–7). The rate of the reaction was strongly dependent upon the nature of the counterion, tetraalkylammonium ions being strong inhibitors of the reaction (rate ratio $K^+/Bu_4N^+ > 10^3$). This specific cation effect was assumed to influence the rate of the ET step (1), presumably *via* an ion pairing mechanism.

$$ArCH_3 + M^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArCH_3^{+\cdot} + M \qquad (1)$$

$$ArCH^{+\cdot} + B: \xrightarrow[\text{slow}]{k_2} ArCH_2^{\cdot} + BH^+ \qquad (2)$$

$$ArCH_2^{\cdot} + M^+ \xrightarrow{\text{fast}} ArCH_2^+ + M \qquad (3)$$

In principle, it should have been possible to estimate $k_1$, the rate constant for forward electron transfer of eqn. (1) from a plot of $1/k_{obs}$ *vs.* 1/[base]. However, due to the slowness of the proton transfer step and a reaction order in base of *ca.* 1.5 at high base concentrations ([$AcO^-$] > 0.25 M) this procedure was not wholly adequate. A $k_1$ value of $\approx 1\ M^{-1}\ s^{-1}$ *can* be obtained from rate data in the region of [$AcO^-$] between 0.04 and 0.25 M, but it carries a large error, $\log k_1 = 0.0 \pm 0.8$.

This difficulty was avoided in recent studies[6,7] of side-chain substitution in methylaromatics by Fe(III)phenanthroline complexes in acetonitrile where both the higher $E^\circ$ of the oxidants (>1.3 V) and higher basicity of the bases employed (pyridine and alkylpyridines) combine in making $k_1$ estimates reliable. From these results, it was concluded that the Marcus theory of outer-sphere electron transfer gives an adequate theoretical description of these processes.

To extend our own investigations to cases where the ET step may become rate-determining, a heteropoly ion of higher oxidation potential was needed to allow for the oxidation of alkylaromatic substrates, more difficultly oxidizable than 4-methoxytoluene. The corresponding radical cations react much faster in the proton abstraction step, as seen from the $\log k_2/E^\circ$ ($ArCH_3^{+\cdot}/ArCH_3$) correlation of Fig. 2, which uses rate data for aqueous solution only.[8] An analogous dependence of rate of bond cleavage of *anion* radicals upon $E^\circ$ for reduction of the parent compounds has been noted.[9]

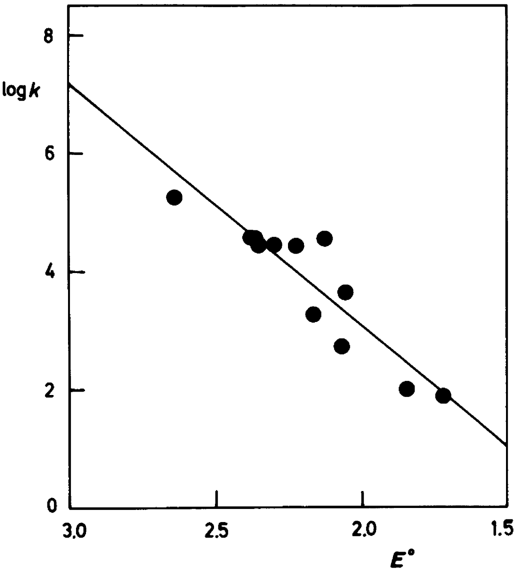

*Fig. 2.* Plot of $\log(k/M^{-1}\ s^{-1})$ *vs.* $E^\circ/V$ for proton abstraction from alkylaromatic radical cations by water. Data were taken from Refs. 8b and 21. The regression lines is $\log k = -5.03 + 4.05\ E^\circ$ ($r$ = 0.92).

Several promising candidates exist, such as $[Ni(IV)Mo_9O_{32}]^{6-}$,[10,11] $[Mn(IV)Mo_9O_{32}]^{6-}$,[10,11] and $[Ce(IV)Mo_{12}O_{42}]^{8-}$,[12] and the Ce(IV) ion (in the following to be abbreviated by Ce(IV)Mo; see Fig. 1) was deemed the most suitable one in view of the fact that the mechanism of Ce(IV) oxidation of alkylaromatics has been extensively explored,[13] generally with $[Ce(IV)(NO_3)_6]^{2-}$ as the oxidant.[13d–n] An ET mechanism of the type given in eqns. (1)–(3) has been shown to be valid, as could also be made plausible by a Marcus type analysis.[14] Moreover, the Ce(IV)Mo/Ce(III)Mo couple is distinctly of the one-electron variety, as far as the central atom is concerned, whereas both the Ni(IV) and Mn(IV) heteropoly ions can utilize two rather closely spaced one-electron transfer steps.

In what follows, a kinetic study of the reaction between Ce(IV)Mo and a series of alkylaromatic hydrocarbons in 50/50 (v./v.) HOAc/$H_2O$ is described. This system indeed behaves as if the $k_1$ step of eqns. (1)–(3) is the rate-determining one, but a detailed analysis according to the Marcus theory[14,15] shows that another mechanism, concerted proton/electron transfer from $ArCH_3$ to Ce(IV)Mo, is a more likely possibility.

## Results

*General remarks.* Ce(IV)Mo is only slightly soluble in water or acetic acid/water mixtures and is insoluble in glacial acetic acid. Since the alkylbenzenes studied also have a limited solubility in water-containing media, there is only a narrow solubility window available for experimentation which severely limits variation of the reaction conditions. Eventually, it was found that a 50/50 (v./v.) HOAc/$H_2O$ medium was the best compromise between the various conflicting requirements.

Addition of acetate ion could only be performed as its tetraalkylammonium salts since all alkali metal and group II ions cause precipitation of Ce(IV)Mo salts. Therefore tetrabutylammonium hydrogen diacetate ($Bu_4N[AcO]_2H$) had to be used as a source of base, in spite of the additional complications introduced (see below).

The solubility behaviour of Ce(IV)Mo is quite different from that of $[Co(III)W_{12}O_{40}]^{5-}$ which tolerates a much wider range of solvent composition and the presence of a large variety of counterions in high concentration.

*Stoicheiometry.* A detailed product study was carried out for the oxidation of *p*-xylene under the same conditions as those normally employed in the kinetic runs (50.0 °C, 50/50 HOAc/$H_2O$, $[ArCH_3]/[Ce(IV)Mo] = 50$). It turned out that the major product, 4-methylbenzyl alcohol, was sensitive toward autoxidation during the reaction and especially during the work-up procedure,* and hence protection from air by argon was necessary. To illustrate this problem an argon protected run followed by work-up without protection from air gave 4-methylbenzyl alcohol (19 %), 4-methylbenzaldehyde (11 %), and 4-methylbenzoic acid (27 %), all yields being calculated on the basis of a consumption of 2 mol of Ce(IV) per mol of product. Contrasting, a completely argon-protected experiment gave 4-methylbenzyl acetate (14 %), 4-methylbenzyl alcohol (55 %) and small amounts only (1–2 %) of the aldehyde and carboxylic acid.

The sum of yields of alcohol, aldehyde and acid are almost identical in the two cases (57 and 56–57 %, respectively).

Addition of acetate ion (10 mM) or increase of the temperature to that of reflux (~100 °C) did not change yields or product distribution significantly. Runs in glacial acetic acid under heterogeneous conditions gave only trace amounts of the acetate (~0.1 % yield), presumably due to the extreme insolubility of the ammonium salt of Ce(IV)Mo in this medium.

To further check the possibility of small systematic errors in the rate constants being due to further oxidation of the benzylic alcohol formed, *p*-xylene and its oxidation products were singled out for a closer study. Under the standard conditions given above the rate constants of *p*-xylene, 4-methylbenzyl acetate, and 4-methylbenzyl alcohol were 0.188, 0.018, and 0.052 $M^{-1}\ s^{-1}$, respectively. These data show that overoxidation cannot be a significant problem in the presence of a large excess of substrate over Ce(IV)Mo, both acetate and alcohol being more difficult to oxidize than the hydrocarbon (see below). Since the anodic oxidation of *p*-xylene in glacial acetic acid is known[17] to give products *via* secondary attack in the second methyl group, a search for such products was performed but gave no indications of any being formed.

The stability of Ce(IV)Mo in 50/50 acetic acid/water at 50 °C was checked by monitoring the absorbance of a $7.5\times10^{-4}$ M solution at 410 nm, no change being noticeable during a period exceeding 3–4 half-lives of the least reactive substrate. The same behaviour was found with acetate ion (8.7 mM) present.

*Cyclic voltammetry.* A cyclic voltammogram of 3 mM Ce(IV)Mo in HOAc/$H_2O$ (1:3) (graphite electrode, no supporting electrolyte added) showed the characteristic behaviour of a heteropoly ion (Fig. 3). Five redox couples (I–V) are seen in the potential region between 0.24 and 1.94 V and among these, the Ce(IV)Mo/Ce(III)Mo couple (I) is the one of immediate interest

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*Other Ce(III) complexes have been shown to catalyze the autoxidation of aromatic side-chains.[16]

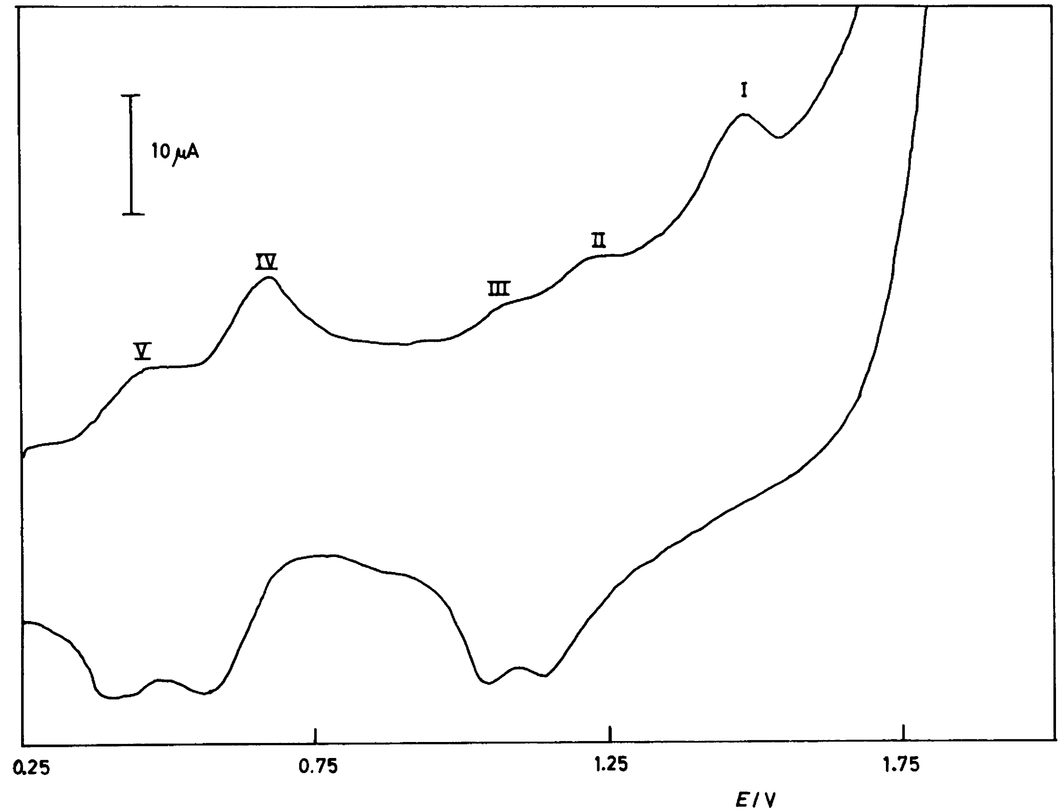

*Fig. 3.* Cyclic voltammogram of Ce(IV)Mo (3 mM) in water/HOAc (3:1) at a sweep rate of 50 mV $s^{-1}$. Electrode material: Graphite. No supporting electrolyte was added.

here. The remaining ones (II–IV) represent successive additions of electrons to the molybdenum oxide shell and thus formation of a Heteropoly Blue.[1]

The $E_{pa}$/V, $E_{pc}$/V and ($E_{pa}-E_{pc}$)/mV values for couples I–V were as follows: I, 1.485, not distinguishable, undefined; II, 1.235, 1.135, 100; III, 1.09, 1.035, 55; IV, 0.67, 0.55, 120; V, 0.47, 0.405, 65. The failure to observe a distinct cathodic peak for I is due to interference from water reduction, and it is therefore not possible to obtain an accurate $E_{pc}$ value of I. However, it must be placed between the $E_{pa}$ values of I and II, and a reasonable estimate is midway between them, or at 1.36 V. This gives ($E_{pa}-E_{pc}$) of I equal to 125 mV and the position of the reversible potential at 1.42 V which we shall take as the $E°$ value of Ce(IV)Mo/Ce(III)Mo in the discussion.

Irreversible $E_{pa}$ values of 4-methylbenzyl alcohol and 4-methylbenzyl acetate were determined in acetonitrile/0.1 M tetrabutylammonium tetrafluoroborate at 2.34 and 2.49 V, respectively, distinctly higher than that of *p*-xylene (2.18 V). Under the same conditions, the $E_{pa}$ of 4-methylbenzaldehyde could not be determined due to merging of the cyclic voltammogram with that of the solvent/supporting electrolyte.

*Kinetics and data treatment.* The kinetics of disappearance of [Ce(IV)Mo] were monitored by recording the absorbance at 410 nm as a function of time, data points being collected automatically at regular intervals and stored on tape. All runs were made under pseudo-first-order conditions with a ratio of $[ArCH_3]_0/[Ce(IV)Mo]_0 \geq 37.5$. *p*-Xylene was singled out as a model compound for a study of the effect of concentration changes and additives; its choice was dictated by its relatively low $E°$ and the wealth of knowledge already available for the ET oxidation of this hydrocarbon.[3,6,11,17,18]

Application of the steady-state approximation to $[ArCH_3^{+\cdot}]$ of eqns. (1)–(2) gives the rate expression of eqn. (4). For the case that the $k_2$

$$-\frac{d[M^+]}{dt} = \frac{k_1k_2[M^+][B:][ArCH_3]}{k_{-1}[M] + k_2[B:]} \qquad (4)$$

step is rate-determining ($k_{-1}[M] \gg k_2[B:]$) an expression directly relating absorbance and time was derived earlier,[5] leading *via* a non-linear regression treatment to the determination of a parameter ($P$), of the appearance given in eqn. (5). If $k_1$ is rate-determining ($k_{-1}[M] \ll k_2[B:]$), eqn.

$$P = \frac{k_1k_2[ArCH_3][B:]}{k_{-1}[M^+]_o + k_2[B:]} \qquad (5)$$

(4) simplifies to eqn. (6), *i.e.*, strict second-order behaviour is observed. Thus it should be possible to determine $k_1$ under pseudo first-order conditions. Computation of $k_1$ was performed by direct

$$d[M^+]/dt = k_1[ArCH_3][M^+] \qquad (6)$$

fitting of absorbance/time data (normally 80–130 data pairs) to an exponential function [(eqn. 7)], using the non-linear regression method developed by Marquardt.[19] Here $k_{obs} = 2k_1[ArCH_3]$ [note the second fast ET step of eqn. (3)] and $f_\infty$ ($f$ denotes absorbance) are the parameters to be determined.

$$f = f_\infty + (f_o - f_\infty)\exp(-k_{obs}t) \qquad (7)$$

Since the kinetic model of eqn. (4) demands inverse first-order dependence of $P$ with $[Ce(IV)Mo]_o$, we first checked the influence of varying the initial concentration of this species. As seen from Table 1, there is no significant dependence of $k_{obs}$ upon $[Ce(IV)Mo]_o$. All calculations of $k_{obs}$ were then based upon eqn. (7), generally giving a very good fit to experimental data (sum of standardized square residuals $(2-10)\times10^{-6}$, random distribution in residual plots). All rate constants are mean values of 3–5 independent runs. The parameter range at the 95 % confidence level was ± (2–4) %, except for the case of toluene, where it was ±7 %.

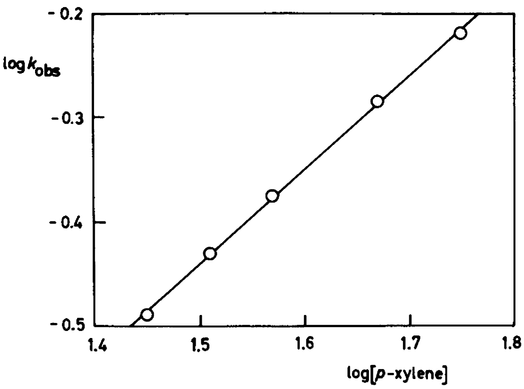

*Fig. 4.* Plot of $\log(k_{obs}/\mathrm{min}^{-1})$ *vs.* log([*p*-xylene]/mM) (Table 1). The slope of the regression line is 0.9(1).

Fig. 4 shows that $k_{obs}$ is first-order in $[ArCH_3]$, the slope of the regression line being 0.9(1). Addition of tetrabutylammonium hydrogen diacetate, trifluoroacetate or trifluoromethanesulfonate caused a strong decrease in rate (Fig. 5 and Table 1) with no rate-enhancing influence of acetate ion relative to the much less basic trifluoroacetate ion. As already mentioned, the specific cation effect could not be studied for alkali metal or group II ions for technical reasons (precipitation).

*Isotope effects.* A kinetically determined value of $k_H/k_D = 1.5(1)$ was observed for Ce(IV)Mo oxidation of *p*-xylene and its perdeuterio deriva-

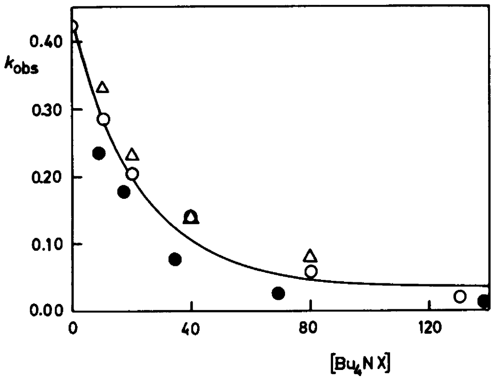

*Fig. 5.* Plot of $k_{obs}/\mathrm{min}^{-1}$ *vs.* $[Bu_4NX]$/mM (Table 1). The curve is the best fitting second-order polynomial through all points. Filled circles, X = $AcO^-$; open circles, X = $CF_3COO^-$; triangles, X = $CF_3SO_3^-$.

*Table 1.* Dependence of $k_{obs}$ (eqn. 7) for oxidation of *p*-xylene by Ce(IV)Mo. Temperature, 50 °C; medium, $HOAc/H_2O$ (50/50).

| [*p*-Xylene]/mM | $[Ce(IV)Mo]_0$/mM | $[Bu_4N^+\ X^-]$/mM | | | $k_{obs}$/min$^{-1}$ |
|---|---|---|---|---|---|
| | | | X | | |
| | | AcO$^-$ | $CF_3COO^-$ | $CF_3SO_3^-$ | |
| 37.5 | 0.56 | | | | 0.39 |
| 37.5 | 0.75 | | | | 0.42 |
| 37.5 | 1.00 | | | | 0.45 |
| 41.8 | 0.75 | | | | 0.60 |
| 39.8 | 0.75 | | | | 0.52 |
| 36.1 | 0.75 | | | | 0.37 |
| 34.6 | 0.75 | | | | 0.32 |
| 37.5 | 0.75 | 8.7 | | | 0.235 |
| 37.5 | 0.75 | 17.3 | | | 0.179 |
| 37.5 | 0.75 | 34.6 | | | 0.076 |
| 37.5 | 0.75 | 69.2 | | | 0.026 |
| 37.5 | 0.75 | 138.4 | | | 0.013 |
| 37.5 | 0.75 | | 10 | | 0.285 |
| 37.5 | 0.75 | | 20 | | 0.204 |
| 37.5 | 0.75 | | 40 | | 0.138 |
| 37.5 | 0.75 | | 80 | | 0.058 |
| 37.5 | 0.75 | | 130 | | 0.021 |
| 37.5 | 0.75 | | | 10 | 0.33 |
| 37.5 | 0.75 | | | 20 | 0.232 |
| 37.5 | 0.75 | | | 40 | 0.138 |
| 37.5 | 0.75 | | | 80 | 0.08 |

*Table 2.* Values of $k_1 = k_{obs}/2/[ArCH_3]$ for the oxidation of methylbenzenes by Ce(IV)Mo (0.75 mM) in $HOAc/H_2O$ (50/50) at 50.0 °C. $[ArCH_3]$ = 37.5 mM.

| Compound | $k_1/10^{-2}$ M$^{-1}$ s$^{-1}$ | $E_0$/V vs. NHE[a] | $\Delta G^{o\prime}$/kcal mol$^{-1}$ [b] |
|---|---|---|---|
| Ethylbenzene | 0.185(5) | 2.51 | 20.5 |
| Toluene | 0.40(3) | 2.64 | 23.5 |
| *m*-Xylene | 1.85(5) | 2.38 | 17.5 |
| *o*-Xylene | 1.85(5) | 2.37 | 17.3 |
| 1,2,3-Trimethylbenzene | 8.6(3) | 2.23 | 14.0 |
| *p*-Xylene | 9.4(3) | 2.30 | 15.7 |
| Mesitylene | 10.3(3) | 2.35 | 16.8 |

[a] Taken from Ref. 21; measured in trifluoroacetic acid.

[b] $\Delta G^{o\prime} = 23.06\,(E^{o}_{Ar} - 1.42) + \dfrac{331.2\ B}{r_{12}\ D}(Z_1 - Z_2 - 1)$, where $Z_1 = -8$, $Z_2 = 0$, $D = 55.4$ and $r_{12} = r_1 + r_2 = 5.6 + 1.7 = 7.3$ Å (see text).

tive, respectively, under the following conditions: 50.0 °C, 50/50 $HOAc/H_2O$, $[ArCH_3]_0$ = 0.0375 M, and $[Ce(IV)Mo]_0 = 7.5 \times 10^{-4}$ M. Essentially the same value was obtained at 40.0 °C [1.6(1)] or in the presence of 8.7 mM acetate ion [1.5(1)].

*Determination of rate constants for a series of methylarenes.* Rate constants for the oxidation of a series of difficultly oxidizable methylarenes ($E^o$ > 2.2 V) by Ce(IV)Mo were determined at 50.0 °C in 50/50 $HOAc/H_2O$ with no base added, $k_1$ being calculated as $k_{obs}/2/[ArCH_3]$ (see Table 2).

## Discussion

The mechanism of the ET mediated oxidation of methylaromatic compounds has been discussed in great detail in recent publications.[5–7,13g–k,20] These were mostly concerned with mechanisms in which the chemical step succeeding electron transfer, proton abstraction [eqn.(2)] or nucleophile attack on the aromatic nucleus, is the rate-determining one. Hence rate constants for the ET step [$k_1$ of eqn. (1)] must be determined by an indirect method involving extrapolation of $1/k_{obs}$ – 1/[base] relationships to 1/[base] = 0.

The case to be discussed here has most of the characteristics of the second extreme of an ET mediated mechanism, namely one in which the initial ET step is rate-determining. Baciocchi *et al.*[13j,k] described borderline behaviour for the cerium ammonium nitrate (CAN) oxidation of alkylaromatics in acetic acid, noting that easily oxidizable substrates (hexamethylbenzene, *p*-methoxytoluene, $E^\circ$ = 1.82 and 1.72 V,[7,21] respectively) underwent slower oxidation upon addition of Ce(III); at the same time the $k_H/k_D$ ratio increased strongly. This effect was ascribed to a switch from ET to proton transfer control of rate [$k_{-1}$ [Ce(III)] changes from being smaller than $k_2$[B] to being equal to or larger than $k_2$[B]; see eqn. (4)]. For more difficultly oxidizable compounds, such as 1,2,3-trimethyl-*tert*-butylbenzene ($E^\circ \sim 2.07$ V by analogy with isodurene), no effect of Ce(III) upon rate or $k_H/k_D$ was noticeable.[13j] The changeover of rate-determining step from ET to proton abstraction was placed between hexamethylbenzene and hexamethylbenzene-$d_{18}$.[13j]

The Ce(IV)Mo oxidations all involve difficultly oxidizable compounds, with $E^\circ$ values well above that of 1,2,3-trimethyl-*tert*-butylbenzene, in fact all above 2.2 V.[24] *p*-Xylene, with $E^\circ$ = 2.30 V, showed the kinetic behaviour expected for an ET controlled rate determining step: No effect of changing $[\mathrm{Ce(IV)Mo}]_o$ and no effect of added base. The products formed are the expected ones for an ET mechanism, once the artefact of aldehyde/carboxylic acid formation by autoxidation during work-up (presumably Ce(III) catalyzed[16]) had been eliminated.

However, a seemingly trivial detail does not fit completely into the picture of a rate-determining ET step. There is still a hydrogen isotope effect, $k_H/k_D$ = 1.5, and this is not affected by added acetate ion. Moreover, the strong rate-inhibiting effect of tetraalkylammonium ions [5,6] upon the ECE reaction scheme [eqns. (1)–(3)] cannot be ascribed to a single step or combination of steps in a consistent manner.

The origin of an isotope effect for an electron transfer step is uncertain. Baciocchi *et al.*[13j] discussed the possibility of a secondary kinetic isotope effect, citing the 5 mV lower $E^\circ$ of hexamethylbenzene-$d_{18}$ rather than that of hexamethylbenzene as a possible cause of a weak such effect (maximally 1.2). It can be added here that the kinetic parameter of the Marcus equation (see below), the reorganization energy $\lambda$, can also in principle be affected by deuterium substitution. Such an effect would operate to make $\lambda$ somewhat smaller in the deuteriated case, a 2 kcal mol$^{-1}$ decrease for example giving rise to a $k_H/k_D$ of *ca.* 0.6 in the region of $\Delta G^{\circ\prime}$ of concern here. These possible changes in $E^\circ$ and $\lambda$ upon deuterium substitution counteract each other and are of course too subtle to lie within reach for experimental determination with present-day techniques.

More serious difficulties arise when one analyzes the rate data of Table 2 in terms of the Marcus theory for outer-sphere electron transfer.[14,15] This treatment expresses $\Delta G^{\neq}$ for an electron transfer step as a parabolic function [eqn. (8)] of $\Delta G^\circ$, the free energy change under the prevailing reaction conditions [corrected by an electrostatic term to give $\Delta G^{\circ\prime}$ as in eqn. (9)] and $\lambda$ = the bond + solvent reorganization energy required to reach the structure of the transition state from the initial collision complex. In eqn. (9), $D$ is the dielectric constant of the medium, $r_{12}$ (in Å) the distance between the reactants in the transition state (approximated with the two reactants as spheres of radii $r_1$ and $r_2$ at collision distance, $r_{12} = r_1 + r_2$, in the simplest model), $Z_1$ and $Z_2$ the charges of the oxidant and reductant, respectively, and $B$ is the usual expression to account for the effect of ionic strength [$\mu$, see eqn. (10)].

$$\Delta G^{\neq} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{\circ\prime}}{\lambda}\right)^2 \tag{8}$$

$$\Delta G^{\circ\prime} = \Delta G^\circ + \frac{331.2\,B}{r_{12}D}(Z_1 - Z_2 - 1) \tag{9}$$

$$B = 10^{-(21.9\, r_{12}\sqrt{\mu/DT})} \tag{10}$$

The following kinetic scheme[22] [eqn. (11)] is then used to describe a complete endergonic electronic transfer step, namely reversible diffusion together of A (acceptor = oxidant) and D (donor = reductant) to form the precursor complex ($k_{12}$ and $k_{21}$), reversible ET within the latter to form the successor complex ($k_{el}$ and $k_{-el}$), and finally the irreversible reaction(s) of the successor complex (summarized in the form of a composite unimolecular rate constant, $k_{30}$). These reactions are 1) dissociation of the successor complex into the free species $A^{-\cdot}$ and $D^{+\cdot}$ and 2) chemical transformations other than back ET ($k_{-el}$) within the successor complex. The unimolecular ET rate constants $k_{el}$ and $k_{-el}$ are then obtained from the Eyring equation [eqn. (12)], where $k\,T/h$ is a universal frequency factor, equal to $6\times10^{12}$ s$^{-1}$ at 25 °C for an elementary process in the gas phase. For a reaction in solution, the frequency factor is usually taken to be 10 times smaller, $6\times10^{11}$ s$^{-1}$.

$$A + D \underset{k_{21}}{\xrightarrow{k_{12}}} (A\ D) \underset{k_{-el}}{\overset{k_{el}}{\rightleftharpoons}} (A^{-\cdot}\ D^{+\cdot}) \xrightarrow{k_{30}} \qquad (11)$$

$$k_{el} = \frac{k\,T}{h}\,e^{-(\Delta G^{\ddagger}/RT)} \qquad (12)$$

Applying the steady state approximation to the concentrations of the precursor and successor complexes eventually gives eqn. (13) for the ET rate constant, $k_1$, where $K_{diff} = k_{12}/k_{21}$ is the equilibrium constant for formation of the precursor complex and $K_{el}$ the equilibrium constant for ET within the precursor/successor complex. It is easily seen that $K_{el} = \exp(-\Delta G^{\circ\prime}/RT)$. Rewriting eqn. (13) in the form of eqn. (14) shows that noticeable kinetic complications due to back ET within the successor complex ensue when $k_{-el} > k_{30}$.

$$\frac{1}{k_1} = \frac{1}{k_{12}} + \frac{1}{K_{diff}\,k_{el}} + \frac{1}{K_{diff}\,K_{el}\,k_{30}} \qquad (13)$$

$$\frac{1}{k_1} = \frac{1}{k_{12}} + \frac{1}{K_{diff}\,k_{el}}\left(1 + \frac{k_{-el}}{k_{30}}\right) \qquad (14)$$

Thus according to eqn. (13) the $\log(k_1)/\Delta G^{\circ\prime}$ curve should consist of (i) a plateau region for sufficiently but not too exergonic reactions ($k_{12}$ is predominant), (ii) a linear region with slope $-1/2.3RT$ for sufficiently endergonic reactions [the third term of eqn. (13) predominates] and (iii) intermediate, parabolic region where $k_{el}$ is the parameter that determines $k_1$. The latter region is centered around $\Delta G^{\circ\prime} = 0$ where the slope of a tangent to the curve has the value $-0.5/2.3RT$.[22b]

In order to first test eqn. (11) with a well-established case of ET-mediated metal ion oxidation, we employed data from the Fe(III)phen$_3^{3+}$, ArCH$_3$ reaction studied by Kochi *et al.*[6,7] This reaction represents a more normal charge situation ([+3,0] $\rightleftharpoons$ [+2,+1]) than the rather unusual one pertaining to the Ce(IV)Mo$^{8-}$, ArCH$_3$ case ([−8,0] $\rightleftharpoons$ [−9,+1]). We might first inquire whether the data set is located in region (ii) of the $\log(k_1)/\Delta G^{\circ\prime}$ curve. This is probed by determining the slope of the straight line that gives the best fit to the data; this turns out to be −0.43(2) mol kcal$^{-1}$, to be compared to the expected one in region (ii), $+1/2.3RT = -0.74$ mol kcal$^{-1}$. This is well outside the limits of experimental error.

Next the experimental data[6,7,21] were fitted to eqn. (13) by non-linear regression, using the reorganization energy λ as the disposable parameter. At an ionic strength of *ca.* 0.1 M, the electrostatic term of eqn. (9) amounted to *ca.* 0.3 kcal mol$^{-1}$; $r_1 + r_2 = 7.0 + 3.5 = 10.5$ Å,[6] $D = 37$. The following values were employed for the remaining constants: $k_{12} = 2\times10^{10}$ M$^{-1}$ s$^{-1}$, $K_{diff} = 0.16$ M$^{-1}$ and the universal frequency factor = $6\times10^{11}$ s$^{-1}$. The value of $k_{30}$ was varied systematically to find the minimum value for which it was at all possible to obtain convergence of the computational procedure. Fig. 6 shows that this lower limit is *ca.* $2\times10^9$ s$^{-1}$ (curve *a*), for which λ

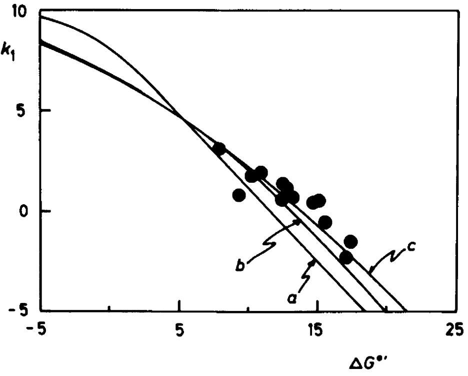

*Fig. 6.* Plots of $\log(k_1/M^{-1}\ s^{-1})$ *vs.* $\Delta G^{\circ\prime}$/kcal mol$^{-1}$ for the oxidation of alkylaromatics by Fe(III)phen$_3$ complexes in acetonitrile at 22 °C. Data were taken from Refs. 6, 7 and 21. The curves represent best fits of the data points to eqn. 13 with $k_{30} = 2\times10^9$ s$^{-1}$ (*a*), $2.8\times10^{10}$ s$^{-1}$ (*b*) and $10^{12}$ s$^{-1}$ (*c*).

= 15(8) kcal mol$^{-1}$) but that no real fit to the data is reached for this value. The meaning of this result is that curve *a* of Fig. 6 to a large extent covers region (ii) and here one would *a priori* not expect any fit. At $k_{30}$ = 2.8×10$^{10}$ s$^{-1}$ (curve *b*), the rate constant for dissociation of the Fe(II)-phen$_3^{2+}$, ArCH$_3^{+\cdot}$ successor complex,[23] one still has not reached the best possible fit ($\lambda$ = 23(15) kcal mol$^{-1}$). Only for $k_{30}$ = 10$^{12}$ s$^{-1}$ is this achieved ($\lambda$ = 23(4) kcal mol$^{-1}$). The same conclusion was drawn by Kochi *et al.* on the basis of a somewhat different analysis:[6] The $k_1$ values of Fig. 6 are influenced by the rate of dissociation of the successor complex to a certain extent, as a result of the endergonicity of the reaction studied, below a certain limit of $k_{30}$.

The model [eqn. (13)] is relatively robust with respect to the choice of the value of the universal frequency factor. With the higher value, 6×10$^{12}$ s$^{-1}$, one obtains essentially the same results as in Fig. 6, except that the best value of $\lambda$ comes out as slightly higher, 30(2) kcal mol$^{-1}$.

Returning to the Ce(IV)Mo oxidation of methylarenes, we first note that the charge product of the successor complex is formally (+1)×(−9) = −9. Using a radius of 5.6 Å for the heteropoly ion and 1.7 Å for ArCH$_3$,* one calculates [23] a rate constant ($k_{30}$) for dissociation of the successor complex at 1.2×10$^6$ s$^{-1}$. Since the underlying model treats the two ions in the successor complex as point charges, this must represent a minimum value.

As a first check, the slope of the best line through the log($k_1$)/$\Delta G^{\circ\prime}$ data was determined to be −0.19 mol kcal$^{-1}$, distinctly different from that expected for region (ii), −0.68 mol kcal$^{-1}$ at 50 °C. Fig. 7 shows the same data (see Table 2) treated in the same way as was done in Fig. 6. The model of the collision complex was the most extreme one possible with respect to electrostatic interactions in the successor complex, with $r_1$ = 5.6 Å and $r_2$ = 1.7 Å, and $k_{12}$, $K_{\mathrm{diff}}$ and the universal frequency factor were taken to be 10$^{10}$ M$^{-1}$ s$^{-1}$, 0.16 M$^{-1}$ and 6×10$^{11}$ s$^{-1}$, respectively. In this case it was only possible to obtain any fit at all for $k_{30}$ > 10$^{11}$ s$^{-1}$ ($\lambda$= 29(20) kcal mol$^{-1}$ at $k_{30}$ = 10$^{11}$ s$^{-1}$ and 29(10) kcal mol$^{-1}$ at $k_{30}$ = 10$^{12}$ s$^{-1}$). Using a value of the universal frequency factor = 6×10$^{12}$ s$^{-1}$ gave essentially the same result.

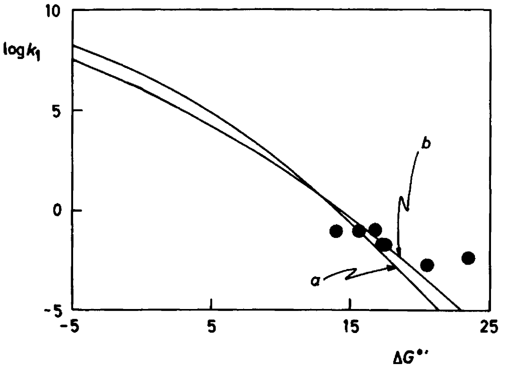

*Fig. 7.* Plots of log($k_1$/M$^{-1}$ s$^{-1}$). *vs.* $\Delta G^{\circ\prime}$/kcal mol$^{-1}$ for the oxidation of alkylaromatics by Ce(IV)Mo in HOAc/H$_2$O (50/50) at 50 °C (Table 2), assuming that the charge of the Ce(IV)Mo heteropoly ion is −8, with $k_{30}$ = 4×10$^{10}$ s$^{-1}$ (*a*) and 10$^{12}$ s$^{-1}$ (*b*).

A closer analysis of the situation for $k_{30}$ ≤ 10$^{11}$ s$^{-1}$ would seem to indicate that the observed rate constants are on the average 5–6 powers of ten *larger* than the ones predicted by the Marcus theory, in combination with the assumption of a rather slow dissociation of the successor complex ($k_{30}$ = 1.2×10$^6$ s$^{-1}$), and thus not represent those of the postulated non-bonded (outer-sphere) ET step ($k_1$). This type of situation is the one expected for a bonded (inner-sphere) ET step, in which one for example might imagine that proton transfer is synchronous with electron transfer [eqn. (14)].

$$\begin{aligned}&\mathrm{Ce(IV)Mo + H{-}CH_2Ar \rightleftharpoons}\\&\mathrm{[Ce(IV)Mo\cdots H\cdots CH_2Ar \leftrightarrow}\\&\mathrm{Ce(III)Mo{-}H\ \dot{C}H_2Ar]^+ \rightarrow Ce(III)Mo{-}H +}\\&\mathrm{ArCH_2^{\cdot}}\end{aligned}\qquad(14)$$

This extreme mechanism has been discussed before in the context of Ce(IV) oxidations,[13n] and is in this form clearly indistinguishable from the more familiar notion of hydrogen atom transfer.

First we must however analyze other possibilities to arrive at values of $k_{30}$ higher than 1.2×10$^6$

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*We prefer a model of the collision complex in which the plane of the aromatic ring is assumed to touch the spheric heteropoly ion. Calculations have also been performed for the model used in Ref. 6 (with $r_2$ = 3.5 Å, corresponding to a situation in which the edge of ArCH$_3$ is assumed to touch the spheric ion); this situation gives almost the same results as those presented in Fig. 8.

$s^{-1}$, and we therefore draw attention to another unusual feature of the Ce(IV)Mo reagent, when used as an oxidant toward neutral substrates. The successor complex will inherently contain a base, the $Ce(III)Mo^{9-}$ ion, which can act as a proton acceptor from the very closely situated radical cation. From what is known about the acidity of $H_8Ce(IV)Mo$ (p*K*:s between 2.2 and 3.0 for the first six dissociating protons and *ca.* 4 and 5 for the two last ones[12]), it is reasonable to ascribe a certain basicity to the $Ce(III)Mo^{9-}$ ion, perhaps corresponding to a p*K* of 4–5 for $Ce(IV)MoH^{8-}$ ion. In such case $k_{30}$ should have a *chemical* contribution considerably larger than $1.2\times10^{6}$ $s^{-1}$, but it is doubtful[8] whether this will be sufficient to reach the critical limit at *ca.* $10^{11}$ $s^{-1}$.

There is also the possibility that protonated forms of $Ce(IV)Mo^{8-}$ are the kinetically active species in the weakly acidic media used. If one for example assumes that $Ce(IV)MoH_3^{5-}$ is the kinetically active species, one can estimate that $k_{30}$ for dissociation of the successor complex is *ca.* $2\times10^{8}$ $s^{-1}$. As seen from Fig. 8, no fit becomes possible until a $k_{30} > 10^{11}$ $s^{-1}$ ($\lambda = 26(47)$ at $10^{11}$ $s^{-1}$ and 25(16) at $10^{12}$ $s^{-1}$) has been reached, and thus this assumption does not provide a solution to the problem.

The CAN study referred to above [13j,k] provides a fairly stringent test of eqn. (13), since it was performed under conditions where electrostatic interactions are expected to be very strong (solvent, acetic acid; $D = 6.3$). With $r_{12} = r_1 + r_2 = 4.6 + 3.5 = 8.1$ Å and $\mu = 0.003$ M, the electrostatic term of eqn. (9) becomes −11.7 kcal $mol^{-1}$. The rate constant for dissociation of the successor complex, for which $Z_1Z_2 = -3$, is estimated[23] to be as low as *ca.* $10^{-3}$ $s^{-1}$. This value might be unrealistically low, but it nevertheless shows that this reaction should behave quite differently from the two others.

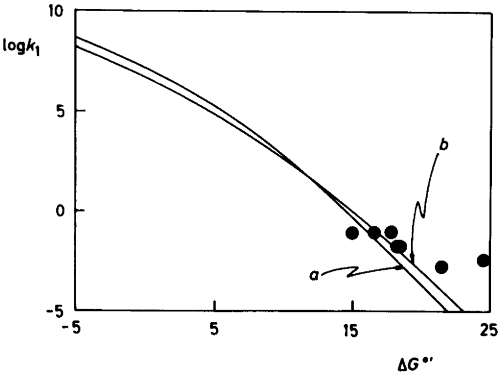

*Fig. 8.* Plots of log($k_1$/$M^{-1}$ $s^{-1}$) *vs.* $\Delta G^{\circ\prime}$/kcal $mol^{-1}$ for the oxidation of alkylaromatics by Ce(IV)Mo in HOAc/$H_2O$ (50/50) at 50 °C (Table 2), assuming that the charge of the Ce(IV)Mo heteropoly ion is −5, with $k_{30}$ = $4\times10^{10}$ $s^{-1}$ (*a*) and $10^{12}$ $s^{-1}$ (*b*).

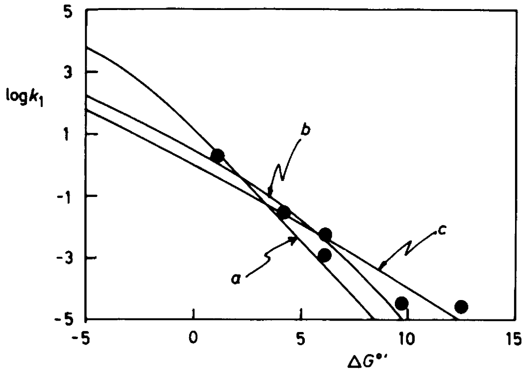

*Fig. 9.* Plots of log($k_1$/$M^{-1}$ $s^{-1}$) *vs.* $\Delta G^{\circ\prime}$/kcal $mol^{-1}$ for the oxidation of alkylaromatics by $Ce(IV)(NO_3)_6^{2-}$ in HOAc at 25 °C, with $k_{30}$ = $10^2$ $s^{-1}$ (*a*), $10^3$ $s^{-1}$ (*b*) and $10^8$ $s^{-1}$ (*c*). Data were taken from Refs. 13j and 13k.

Fig. 9 demonstrates the difference clearly. The lapse into region (ii) behaviour occurs at much lower values of $k_{30}$ than before, between $10^2$ and $10^3$ $s^{-1}$ ($\lambda$ = 57(15) kcal $mol^{-1}$ at $k_{30} = 10^3$ $s^{-1}$ and 60(3) kcal $mol^{-1}$ at $k_{30} = 10^6$ $s^{-1}$). Any assumption that makes $\Delta G^{\circ\prime}$ smaller will decrease the limiting $k_{30}$ value, *e.g.*, to 0.5 $s^{-1}$ ($\lambda$ = 60(10) kcal $mol^{-1}$) for subtraction of 6.9 kcal $mol^{-1}$. It is presently difficult to tell whether any such assumption is reasonable. Although the $k_{30}$ limit changes in the expected direction upon change of the electrostatic situation, it is still too far from the calculated one (5 to 6 powers of 10 too large) to make possible a firm judgment of the usefulness of the Marcus model for CAN oxidation.

Another way of demonstrating the differences between these three reactions is the failure to obtain identical or at least similar values of the reorganization energy of the $ArCH_3^{+\cdot}/ArCH_3$ couple, as is demanded by the Marcus treatment. The reorganization energy of the $Fe(III)phen_3^{3+}$, $ArCH_3$ reaction, 23 kcal $mol^{-1}$, can be obtained as the mean value of the reorganization energies of the self-exchange reactions of the two redox couples involved. Since $\lambda$[Fe(III)phen$_3$/Fe(II)phen$_3$] is 14 kcal mol$^{-1}$,[24] $\lambda$($ArCH_3^{+\cdot}/ArCH_3$) is obtained at 32 kcal mol$^{-1}$. A similar treatment of the Ce(IV)Mo/$ArCH_3$ process is somewhat hampered by the lack of data needed to estimate $\lambda$[Ce(IV)Mo/Ce(III)Mo]. However, reasonably good $\lambda$ values are known for Ce(IV)/Ce(III) in 6 M perchloric[25] and 6 M nitric[26] acid, 66 and 61 kcal mol$^{-1}$, respectively, at 25 °C. Assuming that these values can be ascribed to Ce(IV)$_{aq}$/Ce(III)$_{aq}$ and $Ce(NO_3)_6^{2-}/Ce(NO_3)_6^{3-}$, respectively, they should first be converted to their "intrinsic values" by the method given by Pelizzetti *et al.*,[27] using the "averaged" method by Haim and Sutin[28] to correct for the effect of high ionic strength. The intrinsic values were then calculated to be 52 and 54 kcal mol$^{-1}$, identical within the limits of experimental error.

It is by no means obvious that the Ce(IV)Mo/Ce(III)Mo self-exchange reaction should have the same $\lambda$ as the above-mentioned Ce(IV)/Ce(III) couples, but we see no good alternative by which this value can be estimated. The cyclic voltammetry displayed by Ce(IV)Mo/Ce(III)Mo is an indication of a considerably higher $\lambda$ than that of the electrochemically almost reversible 12-tungstocobalt(III/II)ate couple[4,5] ($\lambda_{intrinsic}$ = 23 kcal mol$^{-1}$). Using $\lambda$[Ce(IV)Mo/Ce(III)Mo] = 53 kcal mol$^{-1}$ in combination with that derived from rate data on the Ce(IV)Mo, $ArCH_3$ reaction, 29 kcal mol$^{-1}$, we estimate $\lambda$($ArCH_3^{+\cdot}/ArCH_3$) at 7 kcal mol$^{-1}$, much lower than that obtained from the Fe(III)phen$_3$, $ArCH_3$ data.

Proceeding to the $Ce(NO_3)_6^{2-}$, $ArCH_3$ reaction, conducted in acetic acid and with an experimentally derived $\lambda$ of 69 kcal mol$^{-1}$, the $\lambda$($ArCH_3^{+\cdot}/ArCH_3$) value comes out as being high, 67 kcal mol$^{-1}$, much higher than for the two other reactions. Here one actually predicts a *lowering* of the $\lambda$ value in changing medium from one of a high dielectric constant to one of low dielectric constant, at least when calculated by the simplest available expression for the solvent reorganization energy.[29] In the particular case of $\lambda$($ArCH_3^{+\cdot}/ArCH_3$), the lowering should be >10 kcal mol$^{-1}$ in going from 50/50 HOAc/water to HOAc. It is, however, only fair to add that the experimental $\lambda$ is rather sensitive toward changes of $\Delta G^{\circ\prime}$ in the endergonic direction, an addition of a mere 4.6 kcal mol$^{-1}$ lowering $\lambda$ to 42(4) kcal mol$^{-1}$ (of course at the expense of having to accept a higher $k_{30}$ limit, $\approx 2.5\times10^7$ s$^{-1}$). This conflicts strongly with our previous analysis, but gives $\lambda$($ArCH_3^{+\cdot}/ArCH_3$) = 31 kcal mol$^{-1}$.

Summarizing, the established[6,7] ET mechanism of the (Fe(III)phen$_3$/$ArCH_3$ reaction gives $\lambda$($ArCH_3^{+\cdot}/ArCH_3$) = 32 kcal mol$^{-1}$ while values of 7 and 67 kcal mol$^{-1}$ are derived from data of the Ce(IV)Mo and CAN oxidations. Is a value of $\lambda$($ArCH_3^{+\cdot}/ArCH_3$) around 32 kcal mol$^{-1}$ in agreement with expectations? In view of the fact that many simple $ArH^{+\cdot}/ArH$ (including heteroaromatics) have low $\lambda$ values,[14] 5–15 kcal mol$^{-1}$, it is difficult at first sight to single out features of the $ArCH_3^{+\cdot}/ArCH_3$ reaction that can explain this difference, which must reside predominantly in the bond reorganization term of $\lambda$ (solvent reorganization energies should be approximately equal in the two cases). A recent ESR study[30] of alkylbenzene radical cations might give a clue: A strong $\sigma$–$\pi$ delocalization (hyperconjugation, manifested in the unexpectedly large hyperfine coupling constant to the methyl hydrogens of 12–18G) donates electrons from the $\sigma$ C$-$H orbitals into the ring, and might well result in a substantial bond length/angle change around the methyl group in going from $ArCH_3^{+\cdot}$ to $ArCH_3$. High $\lambda$ values are similarly observed for other types of compounds where the incipient charge must be largely localized into $\sigma$ bonds (*e.g.*, alkylmetals,[31] alkyl halides,[32] diacyl peroxides,[33] carbanions,[34] aliphatic amines[35] and excited states of anion radicals[36]). We thus think that the question posed above can be answered positively, from which follows that the Ce(IV)Mo/$ArCH_3$ reaction probably does not follow an ET mechanism.

For reactions where one can observe experimentally the kinetic effect of the proton transfer step succeeding the ET equilibrium (12-tungstocobalt (III)ate oxidation of 4-methoxytoluene,[5] CAN oxidation of alkylaromatics,[13j,k] and Fe(III)phen$_3$ oxidation of reactive alkylaromatics[6] and 4-methoxytoluene[7]) the problem of establishing the mechanism is easily resolved in at least one respect; the reaction must take place in at least two steps. For Ce(IV)Mo oxidation, base addition has no effect upon rate, and thus a mechanism involving a synchronous electron/proton transfer step [eqn. (14)] is feasible in principle. The fast proton transfer step within the successor complex discussed above is a starting assumption, the logical extension of which is to bypass the intermediate radical cation and thus couple

ET to motion of a proton. Perrin[37] has analyzed this extreme situation and showed that such a mechanism should give rise to a linear free energy relationship of the Brønsted type with $\alpha \approx 0.5$ over a wide range of reactivity. The Ce(IV)Mo reaction treated in this way has $\alpha = 0.19/0.68 = 0.28$, whereas the Fe(III)phen$_3$ and CAN reactions, known to behave in accordance with the mechanism of eqns. (1)–(3), have $\alpha = 0.43/0.73 = 0.59$ and $0.45/0.73 = 0.62$. Presently, no firm conclusions can be drawn from these values, and only more experimentation aimed at critical examination of the concerted mechanism will resolve the problem.

*Summary and conclusions.* The electron transfer mediated oxidation of alkylaromatic compounds is commonly assumed to proceed according to the mechanism depicted in eqns. (1)–(3). One extreme variety of this scheme has the ET step ($k_1$) as the rate-determining one, and this situation has seemingly been realized in this study by use of the strongly oxidizing heteropoly ion, Ce(IV)Mo, and substrates that lead to highly reactive radical cations ($E^\circ > 2.2$ V).

A distinct feature of heteropoly ions is their high negative charge. Due to their large size, the surface charge density is, however, to be considered low in relation to smaller ions of lower charge, and thus their electrostatic properties are probably not as extreme as is indicated by estimates of diffusion rates and equilibrium constants, based on current theory which treats ions as point charges.

Ce(III)Mo, with a charge of $-9$, is expected to form a rather stable ion pair with $ArCH_3^{+\cdot}$ in the successor complex. If this complication is included in the Marcus treatment, a strict acceptance of the value of the calculated ion pair dissociation constant leads to the conclusion that the rate data are not in accordance with the Marcus theory, predicting rate constants 5–6 orders of magnitude smaller. Even with the higher dissociation rate constants that are possible because of the electrostatic peculiarity of the heteropoly ion, the limit for Marcus behaviour is not reached without unreasonable assumptions.

With this conclusion, logic dictates the necessity of considering a synchronous electron/proton transfer step, as recently suggested by Perrin in a thought-provoking article.[37] While the rate data for the Ce(IV)Mo reaction do not quantitatively agree with Perrin's prediction of an $\alpha = 0.5$ for such a mechanism, we think this alternative must be seriously considered, as also proposed for other systems.[38]

## Experimental

*Materials.* $(NH_4)_6H_2[Ce(IV)Mo_{12}O_{42}]\ 10H_2O$ was prepared according to a published procedure[1b,12] and recrystallized twice from sulfuric acid (2 %). Tetrabutylammonium hydrogen diacetate 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 residue was recrystallized twice from ethyl acetate. Water was of doubly quartz-distilled quality. All other chemicals were of highest commercial quality available and were checked for reducing impurities in blind runs with Ce(IV)Mo before use.

*Stoicheiometry.* A solution (100 mL) of *p*-xylene (37.5 mM) and Ce(IV)Mo (0.75 mM) in acetic acid/water (50/50, v/v) was kept at 50 °C for 2 h under an argon atmosphere. The solution was worked up under argon protection by adding it to sodium hydrogen carbonate solution, followed by ether extraction. Yields were determined by GLC analysis.

*Kinetics.* A solution of Ce(IV)Mo was placed in a cuvette (3.00 mL) in the thermostated (50.0±0.1 °C) compartment of a Cary 219 UV/vis spectrophotometer, equipped with a Digital Interface Port and connected to an HP-85 microcomputer. After thermal equilibration, the reaction was initiated by addition of substrate solution (200 μL) and the absorbance at 410 nm was recorded as a function of time, 80–130 data pairs being collected in each run and stored on tape. Calculation of rate constants were based on eqn. (7), using the non-linear regression method developed by Marquardt[19] on an HP-9835 table-top computer. Errors are given as the range of variation of parameters at the 95 % confidence level.

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