7106 *J. Org. Chem.* **1993**, *58*, 7106–7110

# Side-Chain Oxidation of α-Substituted 4-Methoxytoluenes by Potassium 12-Tungstocobalt(III)ate. The Effect of α-Substituents on the Formation and Deprotonation of the Intermediate Cation Radicals

Enrico Baciocchi,* Massimo Bietti, and Mario Mattioli

*Dipartimento di Chimica, and Centro C.N.R. di Studi sui Meccanismi di Reazione, Universita "La Sapienza" Piazzale A. Moro 5, 00185 Roma, Italy*

*Received June 28, 1993*•

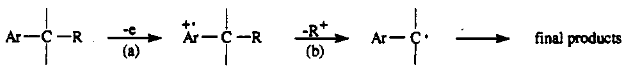
A kinetic study of the side-chain oxidation of α-substituted 4-methoxytoluenes (4-MeOPhCH$_2$R, R = H, Me, OH, OMe, OAc, CN) by $K_5Co^{III}W_{12}O_{40}\cdot 11H_2O$ (Co(III)W) in AcOH/H$_2$O (55:45) has been carried out. The reactions follow complex kinetics, suggesting that both the electron transfer and the radical cation deprotonation steps influence the reaction rate. A careful kinetic analysis has allowed the determination of the values of $k_1$, the rate constant for the electron transfer step, and of $k_{-1}/k_2$, the ratio between the rate constant of the back electron transfer and the one of the deprotonation of the cation radical. A satisfactory Marcus correlation between $k_1$ and the free energy changes for the electron-transfer step is obtained, affording a value of 41 kcal mol$^{-1}$ for the intrinsic barrier of the process. Therefrom a value of 57 kcal mol$^{-1}$ for the reorganization energy pertaining to the conversion of 4-MeOPhCH$_2$R into 4-MeOPhCH$_2$R$^{+\cdot}$ can be calculated. By assuming that $k_{-1}$ is constant (the back electron transfer should be diffusion controlled for all substrates), the relative rate constants for the deprotonation of the radical cations, $k_2$(R)/$k_2$(H), can be obtained by the $(k_{-1}/k_2)_H/(k_{-1}/k_2)_R$ ratios. It has been observed that $k_2$(R)/$k_2$(H) increases by increasing the oxidation potential of the substrate, whereas the reverse occurs with $k_1$. The effect on $k_1$ is, however, much larger than on $k_2$(R)/$k_2$(H), which allows us to conclude that α-substituents influence the oxidation rate of 4-methoxytoluene mainly through the effect exerted on the rate of the electron-transfer step.

The side-chain oxidation of alkyl aromatic compounds is one of the most important organic reactions and accordingly, it has been the subject of intense investigation ever since, both from the practical and the theoretical point of view. In particular, the oxidations occurring by an electron-transfer mechanism have recently attracted the most attention,[1] since they exhibit very interesting properties with respect to the inter- and intramolecular selectivity. In these reactions the electron transfer leads to an aromatic cation radical, which then undergoes the cleavage of a C–R β-bond (in most cases R = H) to form a benzyl radical, oxidized further to the final products (Scheme I).

The structure of the side chain, of course, plays a fundamental role in these reactions. As a matter of fact, it can influence the rate of both the electron transfer and the C–R bond cleavage (steps a and b in Scheme I), as well as determine the nature of the products. However, little information in this respect is presently available, whereas it would certainly be of great importance for a better understanding of the general mechanism of electron-transfer oxidations and, in particular, of the actual role played by the fragmentation step b.

To address the problem, we have therefore carried out a detailed kinetic study of the oxidation of a number of α-substituted 4-methoxytoluenes (4-MeOPhCH$_2$R, with R = H, Me, OH, OMe, OAc, CN) by potassium 12-tungstocobalt(III)ate, $K_5[Co^{III}W_{12}O_{40}]\cdot 11H_2O$, for the sake of simplicity from now on indicated as Co(III)W. This complex has been shown to have excellent properties as an outer sphere one-electron oxidant[2,3] and its reaction with 4-methoxytoluene in AcOH/H$_2$O has already been investigated and shown to occur by the mechanism described in eqs 1–3 (R = H, Ar = 4-MeOPh, X = OH, OAc).[3]

**Scheme I**



$$\text{ArCH}_2\text{R} + \text{Co(III)W} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Ar}^{+\cdot}\text{CH}_2\text{R} + \text{Co(II)W} \qquad (1)$$

$$\text{Ar}^{+\cdot}\text{CH}_2\text{R} + \text{AcO}^- \xrightarrow{k_2} \text{Ar}\dot{\text{C}}\text{HR} + \text{AcOH} \qquad (2)$$

$$\text{Ar}\dot{\text{C}}\text{HR} + \text{Co(III)W} + \text{HX} \longrightarrow \text{Ar}\overset{\overset{\displaystyle \text{X}}{|}}{\text{C}}\text{HR} + \text{Co(II)W} + \text{H}^+ \qquad (3)$$

It was anticipated that a careful analysis of the kinetic results would provide us with reliable information concerning the role played by the α-substituents in the two fundamental steps of the oxidation process. The results of this study are presented in this paper.

## Results

The reactions of Co(III)W with 4-MeOPhCH$_2$R have been carried in 55/45 (w/w) AcOH/H$_2$O mixed solvents at 50 °C, in the presence of 0.47 M potassium acetate; under these conditions the reaction follows the stoichiometry indicated in Scheme II (X = OH, OAc). Side-chain substituted products are formed when R = H, Me. With R = OH, OMe, OAc, however, the only observed reaction product is 4-methoxybenzaldehyde, presumably derived

---

• Abstract published in *Advance ACS Abstracts,* October 15, 1993.

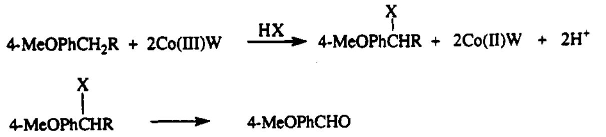
[1] See for example: Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981. Minisci, F.; Citterio, A.; Giordano, C. *Acc. Chem. Res.* **1983**, *16*, 27. Baciocchi, E.; Ruzziconi, R. *Free Radicals in Synthesis and Biology;* Minisci, F., Ed.; NATO ASI Series, Kluwer: Dordrecht, 1989; p 155. Sydnes, L. V.; Hansen, S. H.; Burkow, I. C.; Saethre, L. J. *Tetrahedron* **1985**, *41*, 5205.

[2] Eberson, L. *New J. Chem.* **1988**, *16*, 151.

[3] Eberson, L. *J. Am. Chem. Soc.* **1983**, *105*, 3192.

0022-3263/93/1958-7106$04.00/0

**Scheme II**



$$\text{4-MeOPhCH}_2\text{R} + 2\text{Co(III)W} \xrightarrow{\text{HX}} \text{4-MeOPhC}\overset{\text{X}}{\text{H}}\text{R} + 2\text{Co(II)W} + 2\text{H}^+$$

$$\text{4-MeOPhC}\overset{\text{X}}{\text{H}}\text{R} \longrightarrow \text{4-MeOPhCHO}$$

by hydrolysis of the first formed α-hydroxy- and α-acetoxy-substituted derivatives. When R = CN, both the α-acetoxy derivative and 4-methoxybenzaldehyde are formed.

Kinetics have been carried out spectrophotometrically by following the decrease of the absorption due to Co(III)W at 390 nm. In all cases, the concentration of Co(III)W (between $2.5 \times 10^{-4}$ and $9.4 \times 10^{-4}$) has been at least 100-fold smaller than that of the substrate. As expected on the basis of results for the reaction of Co(III)W with 4-methoxytoluene,[3] the reactions do not follow simple first-order kinetics, deviation from the first-order law increasing with the progress of the reaction. This is due to a retarding effect of Co(II)W, which has been confirmed by carrying out experiments in the presence of this species. Thus, the electron-transfer step (eq 1) is (at least) partially reversible and the deprotonation step (eq 2) is kinetically significant. It has been therefore necessary to use the complete rate expression (eq 4) derived for the

$$\frac{-d[\text{Co(III)W}]}{dt} = \frac{2k_1k_2[\text{ArCH}_2\text{R}][\text{Co(III)W}][\text{AcOK}]}{k_{-1}[\text{Co(II)W}] + k_2[\text{AcOK}]} \qquad (4)$$

mechanism in eqs 1–3, where the rate of the back electron transfer cannot be disregarded in comparison with that of the radical cation deprotonation and vice versa.

A mathematical analysis of this equation has been provided by Kochi and co-workers[4-6] for the case of the oxidation of methylbenzenes by iron(III) phenanthrolines. Following such analysis the expression reported in eq 5 is obtained,

$$-\ln x - a(1 - x) = bt \qquad (5)$$

where $x$ is the extent of reaction, measured by $(A_t - A_\infty)/(A_0 - A_\infty)$; $A_t$ is the absorbance at a given time $t$, $A_\infty$ the final absorbance, $A_0$ the absorbance at $t_{\text{exp}} = 0$ and $a$ and $b$ are given by eqs 6 and 7, respectively.

$$a = pG/(p + 1) \qquad (6)$$

$$b = 2k_1[\text{ArCH}_2\text{R}]/(p + 1) \qquad (7)$$

In these equations $k_1$ is the rate constant for the electron transfer step (eq 1), $p$ is given by eq 8 (where $C$ is the analytical concentration of Co(III)W, $k_{-1}$ and $k_2$ are the rate constants of the back electron transfer and the deprotonation reaction, respectively) and $G$, a correction factor, is calculated from eq 9,

$$p = k_{-1}C/k_2[\text{AcOK}] \qquad (8)$$

$$G = \frac{1}{C}\frac{(A_0 - A_\infty)}{(\epsilon_{\text{III}} - \epsilon_{\text{II}})} \qquad (9)$$

where $\epsilon_{\text{III}}$ and $\epsilon_{\text{II}}$ are the extinction coefficients of Co(III)W and Co(II)W, at the monitoring wavelength (1227.1 and 125.2 $\text{M}^{-1}\text{cm}^{-1}$, respectively). The $G$ factor accounts for the fact that at $t_{\text{exp}} = 0$ some reaction may already have occurred.

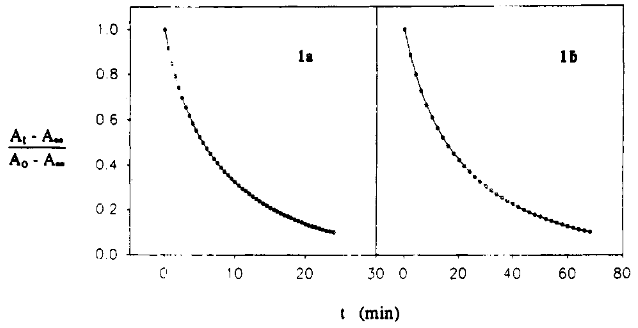


**Figure 1.** Diagrammatic representation of a kinetic run for two substrates (**1a**: 4-methoxybenzyl alcohol; **1b**: 4-methoxybenzyl methyl ether). Circles correspond to the experimental points, and the curves correspond to the best possible fit to the data according to eq 5 (**1a**: $a = 0.567$, $b = 0.0745$; **1b**: $a = 0.605$, $b = 0.0255$).

**Table I. Kinetic Data for the Oxidation of 4-MeOPhCH$_2$R by Co(III)W in AcOH–H$_2$O at 50 °C with 0.47 M AcOK**

| R | $k_1$[a] ($\text{M}^{-1}\,\text{s}^{-1}$) | $k_{-1}/k_2$[b] | $t_{1/2}$[c] (min) | $E^0$[d] (V vs NHE) |
|---|---|---|---|---|
| Me | $1.8 \times 10^{-1}$ | $8.2 \times 10^3$ | 3 | 1.75 |
| H | $9.7 \times 10^{-2}$ | $7.2 \times 10^3$ | 4 | 1.77 |
| OH | $2.1 \times 10^{-2}$ | $1.2 \times 10^3$ | 6.5 | 1.89 |
| OMe | $7.0 \times 10^{-3}$ | $1.1 \times 10^3$ | 20 | 1.91 |
| OAc | $9.8 \times 10^{-4}$ | $2.0 \times 10^3$ | 165 | 1.93 |
| CN | $3.5 \times 10^{-4}$ | $2.7 \times 10^2$ | 240 | 2.00 |

[a] Rate constant for the electron-transfer step (eq 1), calculated as described in the text. [b] Ratio between the rate constant for the back electron transfer and the one for the deprotonation step (eq 2), calculated as described in the text. [c] Time needed to halve the initial concentration of Co(III)W ($9.4 \times 10^{-4}$ M) in the presence of an excess of substrate ($9.4 \times 10^{-2}$ M). [d] Reference 8.

When we have fitted our kinetic data to eq 5 by a multiple nonlinear regression analysis, very satisfactory curve fits have been obtained (two examples are in Figure 1). This supports the mechanism in eqs 1–3 and confirms that both the electron transfer and the deprotonation step contribute to the oxidation rate.

The nonlinear regression analysis provides the values of $a$ and $b$, from which $k_1$ and the $k_{-1}/k_2$ ratio can be calculated by means of eqs 6–9. These values are collected in Table I, together with an estimate of the overall oxidation rate given by the times ($t_{1/2}$) needed to halve the concentration of Co(III)W. In the same table are also displayed the oxidation potentials of the various substrates, evaluated by the h$\nu$ values of the charge-transfer bands of their complexes with tetracyanoethylene, as previously described.[7,8]

## Discussion

The data in Table I show that the rate constant for the electron-transfer step ($k_1$) decreases as the oxidation potential of the substrate increases, in line with expectations.

The relationship between $k_1$ and $E^0$ can be examined in terms of the Marcus equation[9] (eq 10)

---

(4) Schlesener, C. J.; Kochi, J. K. *J. Org. Chem.* **1984**, *49*, 3142.

(5) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3567.

(6) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7472.

(7) Baciocchi, E.; Crescenzi, M.; Fasella, E.; Mattioli, M. *J. Org. Chem.* **1992**, *57*, 4684.

(8) Baciocchi, E.; Del Giacco, T.; Elisei, F. *J. Am. Chem. Soc.*, submitted.

**Table II. Free Energy Changes for the Reaction: $Co(III)W + 4\text{-}MeOPhCH_2R \rightarrow CO(II)W + 4\text{-}MeOPhCH_2R^{+\bullet}$**

| R | $\Delta G^{\circ a}$ (kcal mol$^{-1}$) | $\Delta G^{\circ\prime b}$ (kcal mol$^{-1}$) |
|---|---|---|
| Me | 17.0 | 13.9 |
| H | 17.5 | 14.4 |
| OH | 20.3 | 17.1 |
| OMe | 20.8 | 17.6 |
| OAc | 21.2 | 18.1 |
| CN | 22.8 | 19.7 |

[a] Calculated from eq 12. [b] Calculated from eq 13.

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{\circ\prime}}{\lambda}\right)^2 \tag{10}$$

where $\Delta G^{\ddagger}$ is the activation free energy for the electron-transfer step, $\Delta G^{\circ\prime}$ is the standard free energy for the same step corrected for the electrostatic interaction arising from the charge variation in the reactants upon electron transfer, and $\lambda$ is the reorganization energy, that is the energy required for the adjustments in nuclear geometry and solvation shell which make the electron transfer possible. Since $\Delta G^{\ddagger}/RT = 2.3(\log Z - \log k_1)$, eq 10 can be converted into eq 11 ($Z = 6 \times 10^{11}$), which directly

$$\log k_1 = 11.78 - \frac{\lambda}{9.2RT}\left(1 + \frac{\Delta G^{\circ\prime}}{\lambda}\right)^2 \tag{11}$$

relates the rate constants for the electron-transfer step to the free energy changes.

The $\Delta G^{\circ}$ values have been calculated from eq 12 using the $E^0$ values in Table I and an $E^0$ value of 1.01 V (vs NHE) for Co(III)W[3], whereas $\Delta G^{\circ\prime}$ is given by eq 13,

$$\Delta G^{\circ} = 23.06[E^0_{\text{substrate}} - E^0_{\text{Co(III)W/Co(II)W}}] \tag{12}$$

$$\Delta G^{\circ\prime} = \Delta G^{\circ} + \frac{(Z_1 - Z_2 - 1)e^2 f}{D r_{12}} \tag{13}$$

where $Z_1$ and $Z_2$ are the charges of the oxidant (−5) and the substrate (0), respectively, $e$ is the electron charge, $r_{12}$ is the distance between Co(III)W and the substrate in the encounter complex (taken as 7 Å), $D$ is the dielectric constant of the medium (51.2 for $AcOH/H_2O$ 55/45),[3] and $f$ is a factor which accounts for the ionic strength effect. This factor can be calculated by eq 14, where $\mu$ is the ionic

$$f = 10^{-[21.9 r_{12}(\mu/DT)^{1/2}]} \tag{14}$$

strength (0.49, with 0.47 M AcOK), but, since it is well known that eq 14 overcorrects for high ionic strengths, we have applied the averaged method by Haim and Sutin,[10] thus obtaining an $f$ value of 0.57. The values of $\Delta G^{\circ}$ and $\Delta G^{\circ\prime}$ calculated as described above are reported in Table II.

In Figure 2 a nonlinear least-squares curve fitting of the experimental data ($k_1$ from Table I and $\Delta G^{\circ\prime}$ from Table II) to eq 11 is reported, using the reorganization energy $\lambda$ as an adjustable parameter. The best fit of the experimental data with the curve calculated by eq 11 is obtained for a $\lambda$ value of 41 kcal mol$^{-1}$, which represents the overall (reactants and solvent) reorganization energy associated with the transfer of an electron from 4-MeOPhCH$_2$R to Co(III)W. The fit is very satisfactory and supports the validity of the kinetic analysis used for the calculation of the $k_1$ values.

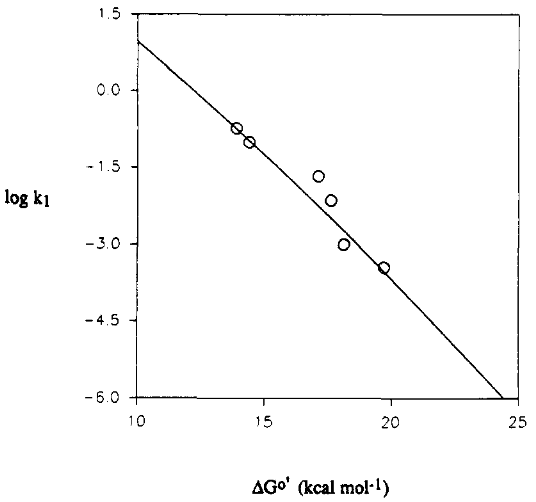


**Figure 2.** Diagram of log $k_1$ vs $\Delta G^{\circ\prime}$ for the reactions of 4-MeOPhCH$_2$R (R = H, Me, OH, OMe, OAc, CN) with Co(III)W in $AcOH/H_2O$ 55:45. Circles correspond to the experimental values; the curve has been calculated according to eq 11 with a $\lambda$ value of 41 kcal mol$^{-1}$.

The reorganization energy for an electron-transfer step is approximately given by the arithmetic average of the reorganization energies of the donor (D) and acceptor (A) self-exchange reactions (eq 15).

$$\lambda_{AD} = \frac{(\lambda_{A/A^{-\bullet}} + \lambda_{D/D^{+\bullet}})}{2} \tag{15}$$

In our case, using a value of 25 kcal mol$^{-1}$ for the reorganization energy associated with the Co(III)/Co(II) couple,[2] it is possible to calculate a value of 57 kcal mol$^{-1}$ for the reorganization energy of the 4-MeOPhCH$_2$R$^{+\bullet}$/4-MeOPhCH$_2$R couple. This value is in excellent agreement with those determined in a number of oxidation reactions of alkyl aromatic compounds[2] and confirms previous results indicating that the reorganization energies for the conversion of an alkyl aromatic to its radical cation are relatively high. As previously discussed,[7] these high reorganization energies have been justified on the basis of the strong hyperconjugative effect of the $CH_3$ group, also confirmed by ESR measurements; however, it is very intriguing that theoretical calculation does not show any substantial difference in the molecular geometry between toluene and toluene radical cation.[7]

Data of Table I show that the $k_{-1}/k_2$ ratio decreases by increasing the $E^0$ value of the substrate. This indicates that relative importance of steps 1 and 2 with respect to the reaction rate changes by changing the oxidation potential of the substrate. Namely, as we move toward less easily oxidizable substrates the kinetic weight of the electron-transfer step progressively increases, whereas that of the deprotonation step increases as we decrease the $E^0$ value of the substrate. The limit case (rate-determining deprotonation) is almost reached with 4-MeOPhCH$_3$.[11]

---

(9) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Eberson, L. *Electron Transfer Reactions in Organic Chemistry;* Springer-Verlag: Berlin, Heidelberg, 1987; Chapter III. (c) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

(10) Haim, A.; Sutin, N. *Inorg. Chem.* **1976**, *15*, 476.

(11) Actually, in the study of this substrate carried out by Eberson[3] the kinetic data were treated by assuming that in eq 4, $k_{-1}[Co(II)W] \gg k_2[AcO^-]$, that therefore the electron-transfer step is fully reversible. A value of $k_1$ between 2–10 M$^{-1}$ s$^{-1}$ was first estimated based on the Marcus theory, which is much higher than that estimated in the present paper. Later a smaller value, 1 M$^{-1}$ s$^{-1}$, was considered more reliable.[12,13] It was recognized, however, that this value too carries high error limits.

**Table III. Data of Relative Reactivity ($k_2$(R)/$k_2$(H)) for the Deprotonation of 4-MeOPhCH$_2$R$^{+\cdot}$ in AcOH/H$_2$O/AcO$^-$**

| R | $k_2$(R)/$k_2$(H)[a] AcOH/H$_2$O/AcO$^-$ | R | $k_2$(R)/$k_2$(H)[a] AcOH/H$_2$O/AcO$^-$ |
|---|---|---|---|
| H | 1.0 | OH | 9.0 |
| Me | 1.4 | OMe | 9.8 |
| OAc | 5.4 | CN | 40.1 |

[a] Calculated from the $k_{-1}/k_2$ ratios (Table I) by assuming that $k_{-1}$ is the same for all substrates (see text). Statistically corrected.

These trends are due to the fact that, as we will see better later, by increasing $E^0$, $k_2$ increases whereas $k_{-1}$ remains practically constant.

Interestingly, the above observation provides a rationale to the previous unexplained finding that in the oxidation of polymethylbenzenes by cerium(IV) ammonium nitrate (a reaction certainly occurring by an electron-transfer mechanism), the deprotonation of the radical cation is partially rate-determining with hexamethylbenzene, whereas the rate is controlled by the electron-transfer step with the less easily oxidizable 5-*tert*-butyl-1,2,3-trimethylbenzene.[12,13,14]

From the $k_{-1}/k_2$ values of Table I, information with respect to the $\alpha$-substituent effects on the fragmentation step can also be obtained. Accordingly, it is possible in principle to calculate the rate constant ($k_2$) for this step, since $k_{-1}$ can be obtained by the known rate constant for the electron transfer step $k_1$, divided by the equilibrium constant $K$, which in turn can be calculated from the $\Delta G°$ value (Table II). However, we are aware that there is considerable uncertainty in the estimated $E^0$ values and consequently in the $\Delta G°$ values derived therefrom. Even though this uncertainty does not substantially affect the logarithmic Marcus plot (which, in addition, is mostly concerned with relative reactivity values), it is expected to significantly influence the absolute value of $K$ and hence of $k_{-1}$ (for example an error as small as 25 mV in the estimate of the $E^0$ value induces a 300% error in $k_{-1}$).

Thus, more than the absolute values of $k_2$, it seems safer to discuss the relative rate constants of deprotonation, $k_2$(R)/$k_2$(H), which can be obtained by assuming that, being that the electron-transfer steps are largely endoergonic in all cases, $k_{-1}$ is always diffusion controlled and has therefore the same value in all of the studied reactions.[15] Values of $k_2$(R)/$k_2$(H), reported in Table III, are thus obtained by dividing the $k_{-1}/k_2$ value for 4-MeOPhCH$_3^{+\cdot}$ by that for 4-MeOPhCH$_2$R$^{+\cdot}$. It can be noted that all substituents increase the rate of deprotonation of 4-MeOPhCH$_2$R$^{+\cdot}$; the effects, however, are not large. Interestingly, they are very similar to those found in the deprotonation of 4-MeOPhCH$_2$R$^{+\cdot}$ induced by NO$_3^-$, where, however, the *absolute* $k_2$ values have been directly measured by a laser photolysis study.[8] This agreement, of course, is a still further proof of the reliability of the information provided by the kinetic approach used in the present work.

The data reported in Table III also clearly show that the deprotonation rate increases as the $E^0$ value of the 4-MeOPhCH$_2$R$^{+\cdot}$/4-MeOPhCH$_2$R couple (Table I) increases, which is quite reasonable since a larger $E^0$ indicates a less-stable cation radical. The phenomenon is, however, more complex, and a detailed discussion of the effect of $\alpha$-substituents on the deprotonation rate of an alkyl aromatic cation radical is reported elsewhere.[8,16]

A final notation is that the effect of the $\alpha$-substituents on the deprotonation of the radical cation is exactly the opposite than the one on the electron-transfer step. However, the latter effect is significantly larger than the former, since a 0.25-V change in $E^0$ induces a 500-fold change in $k_1$, but only a 40-fold change in $k_2$. This allows us to conclude that $\alpha$-substituents influence the rate of an electron transfer side chain oxidation of an alkyl aromatic compound, mainly through their influence on the electron-transfer step, even when the deprotonation rate of the radical cation is kinetically significant. This conclusion, derived from the kinetic analysis, is in line with the observation that the overall oxidation rate (measured by the $t_{1/2}$ values in Table I) decreases on increasing the oxidation potential of the substrate.

## 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. GC-MS analyses were performed on a HP5890 GC equipped with a 12 m × 0.2 mm silica capillary column coated with methylsilicone gum and coupled with a HP5970 MSD. UV/vis spectra were recorded on a Cary 210 and a HP8452 spectrophotometer. Kinetic runs were followed with a Cary 219 and a Cary 1 UV/vis spectrophotometer. $^1$H NMR spectra were recorded on a Bruker WP80 SY spectrometer.

**Materials.** High-purity commercial samples of cobaltous acetate tetrahydrate, sodium tungstate dihydrate, potassium acetate, and potassium persulfate (Fluka) were used as received. Potassium 12-tungstocobalt(III)ate was prepared as described previously.[3] 4-Methoxytoluene, 4-methoxybenzyl alcohol (Merck), and (4-methoxyphenyl)acetonitrile (Fluka) required further purification and were distilled under reduced pressure.

4-Methoxyethylbenzene was prepared from the corresponding ketone by the Huang–Minlon modification of the Wolff–Kishner reduction, purified first by chromatography on a silica gel column (eluent petroleum ether (bp 40–70 °C)/ethyl acetate 10:1) and then by distillation under reduced pressure (bp 85–87 °C at 21 mmHg (lit. 193–194 °C),[17] yield 74%).

4-Methoxybenzyl methyl ether was prepared by reaction of 4-methoxybenzyl alcohol with methyl iodide and sodium hydride in anhydrous tetrahydrofuran. After chromatography on a silica gel column (eluent petroleum ether (bp 40–70 °C)/ethyl acetate 4:1) the product was distilled twice under reduced pressure (bp 47–50 °C at 1.5 × 10$^{-3}$ mmHg (lit. 107–108 °C at 15 mmHg),[18] yield 80%).

4-Methoxybenzyl acetate was prepared by reaction of 4-methoxybenzyl alcohol and acetic anhydride in pyridine and purified by distillation under reduced pressure (bp 64–70 °C at 2.3 × 10$^{-3}$ mmHg (lit. 130–140 °C at 14 mmHg),[19] yield 86%).

**Product Analysis.** The reaction products were as follows (X = OH, OAc): 4-MeOPhCHXCH$_3$ from 4-MeOPhCH$_2$CH$_3$; 4-MeOPhCHO from 4-MeOPhCH$_2$OMe, 4-MeOPhCH$_2$OH and 4-MeOPhCH$_2$OAc; 4-MeOPhCHO and 4-MeOPhCHOAcCN from 4-MeOPhCH$_2$CN.

To establish the reaction stoichiometry a quantitative determination (NMR) of the products was carried out for the reactions of 4-MeOPhCH$_2$OCH$_3$ and 4-MeOPhCH$_2$CN. With the former compound (internal standard triphenylmethane) it was found that 1.88 × 10$^{-3}$ mol of Co(III)W produces 8.5 × 10$^{-4}$ mol of

---

[12] Eberson, L.; Jonsson, L. *Acta Chem. Scand. Ser. B40* **1986**, 79.

[13] Eberson, L.; Nilsson, M. *Acta Chem. Scand. B*, in press.

[14] Baciocchi, E.; Mandolini, L.; Rol, C. *J. Am. Chem. Soc.* **1980**, *102*, 2597.

[15] Actually, by using the $k_1/k_{-1}$ ratios obtained by the $E^0$ values of Table I, values of $k_{-1}$ ranging from 6.4 × 10$^{10}$ to 1.1 × 10$^{12}$ M$^{-1}$ s$^{-1}$ can be obtained. There is no doubt that if we consider the high error limits of these values (see text), these values support the assumption of a back-electron-transfer step which is diffusion controlled, in all cases. See also ref 3.

[16] Baciocchi, E.; Mattioli, M.; Romano, R.; Ruzziconi, R. *J. Org. Chem.* **1991**, *56*, 7154.

[17] Wender, I.; Greenfield, H.; Orchin, M. *J. Am. Chem. Soc.* **1951**, *73*, 2656.

[18] Anglade, M. *Compt. Rend.* **1940**, *210*, 52.

[19] Nyberg, K.; Wistrand, L. *J. Org. Chem.* **1978**, *43*, 2613.

4-MeOPhCHO. With the latter (internal standard 4-MeOPhCH$_2$OCH$_3$), 1.88 × $10^{-3}$ mol of Co(III)W forms 9.1 × $10^{-4}$ mol of products (4.9 × $10^{-3}$ mol of 4-MeOPhCHO and 4.2 × $10^{-4}$ mol of 4-MeOPhCHOAcCN). The amounts expected for a 2:1 stoichiometry (Scheme II) are 9.4 × $10^{-4}$ mol in both cases.

**Measurement of the Kinetics.** All the kinetics studied were carried out in a 1.0-cm quartz cuvette previously flushed with argon; acetic acid and bidistilled water were thoroughly purged with argon. A cuvette, containing the solution of 4-MeOPhCH$_2$R (2.5 × $10^{-2}$ to 9.4 × $10^{-2}$ M) and AcOK (0.47 M) in AcOH/H$_2$O (55/45), was placed in a thermostated compartment of a UV/vis spectrophotometer. After thermal equilibration at 50 °C, the reaction was started by rapid addition of the Co(III)W solution (1.5 × $10^{-3}$ M, 50–200 μL). The rate of disappearance of cobalt(III) was followed spectrophotometrically by measuring the absorbance of Co(III)W at 390 nm. The absorbance $A$ was recorded up to when a constant value was reached ($A_\infty$) and was related to the extent of reaction as $x = [\mathrm{Co(III)W}]/[\mathrm{Co(III)W}]_0 = (A_t - A_\infty)/(A_0 - A_\infty)$ (see text). At least four kinetic runs were performed for each substrate.

For the regression analysis, values of $x$ were taken from 1.0 to 0.1, corresponding to 0–90% conversion, respectively. The regression analysis was performed for each experiment at three different values of $x$ ranging from 1.0 to 0.5, 1.0 to 0.25, and 1.0 to 0.1, i.e. conversions of 50, 75, and 90%, respectively, and the results were an average of these three values. This procedure ensured that uniform kinetics were obtained throughout each kinetic run.[6] In the case of 4-MeOPhCH$_2$OAc we observed that after 70 h in acetic acid/water (55/45) at 50 °C, a significant amount of substrate (20%) was hydrolyzed to the alcohol. For this substrate, only the absorbance data referring to the first 50% of the reaction were used in the kinetic analysis.

**Acknowledgment.** This work has been carried with the financial support of the Ministry of the University and Technological Research (MURST) and the European Community [Contract No. SC1-CT91-0750(TSTS)]. We also thank Prof. L. Eberson for making available a manuscript to us before publication.