Electron-Transfer Reactions in Organic Chemistry. 4. A Mechanistic Study of the Oxidation of *p*-Methoxytoluene by 12-Tungstocobalt(III)ate Ion

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Abstract: A kinetic study of the oxidation of *p*-methoxytoluene by the heteropolyion 12-tungstocobalt(III)ate ($Co^{III}W_{12}O_{40}^{5-}$) in acetic acid/water with an acetate salt present has been performed. The rate of disappearance of the cobalt species is first order in [*p*-methoxytoluene] and [AcO^-] (at [AcO^-] < 0.25 M) and inverse first order in the final concentration of $Co^{II}W_{12}O_{40}^{6-}$. The reaction is strongly affected by the nature of the cation present, the observed rate constant (k_{obsd}) decreasing in the order $Sr^{2+} > Cs^+ > Ca^{2+} > Rb^+ > K^+ > Li^+ > Na^+ > Me_4N^+ > Bu_4N^+ > Pr_4N^+ > Hex_4N^+ > Dec_4N^+$. The effect of solvent composition is to decrease k_{obsd} with decreasing dielectric constant, and k_{obsd} shows a positive salt effect. A relatively strong isotope effect, k_H/k_D = 5–7, indicates proton transfer in the rate-determining step. The Marcus theory has been used to analyze the rate data, and it is concluded that they are best represented by a mechanism involving a reversible electron-transfer step, followed by rate-determining proton abstraction from the radical cation. The forward electron-transfer rate constant is estimated to be 2–10 M^{-1} s^{-1}, the backward electron-transfer rate constant to be $>10^{10}$ M^{-1} s^{-1}, and the rate constant for the proton abstraction step to be 80 (water as base) or 3.6×10^5 (acetate ion as base) M^{-1} s^{-1}. The specific cation effect is most likely due to the cation acting as an electron mediator in the transition state of the electron-transfer step.

The study of metal ion oxidation of organic compounds is a thriving research area, as witnessed by recent books[2] and reviews.[3] Of the possible reaction mechanisms,[2a] initial reversible nonbonded electron transfer followed by a slow chemical step (nucleophilic capture or fragmentation of the intermediate radical cation) is an obvious first mechanistic choice for high-potential metal ions[4] such as Ce(IV), Ag(II), Co(III), Mn(III), and Cu(III), but unambiguous kinetic evidence has so far been obtained for Mn(III)[5] and Ce(IV)[6] only. We have recently[7] reported on the phenomenology of the reactions between the 12-tungstocobalt(III)ate ion ($[Co^{III}W_{12}O_{40}]^{5-}$, in the following to be abbreviated as $Co^{III}W$; see Figure 1) and several types of aromatic compounds in acetic acid media.[8] Generally, the reactivity of this ion closely resembles that of electron-transfer oxidants, such as the anode, Ce(IV) or Ag(II), in that side-chain as well as nuclear acetoxylation can be achieved, even when fluorine is the leaving group (an example of the so-called $S_{ON}2$ reaction[9]). Arylacetic acids are smoothly decarboxylated by $Co^{III}W$,[7] another analogy to electron-transfer oxidants of different types.

From this behavior and a limited study of substituent and isotope effects in the oxidation of 3- and 4-X-toluenes, it was deemed of great interest to fully probe the kinetic properties of $Co^{III}W$ in a specific reaction. $Co^{III}W$ has the cobalt ion deeply buried within a shell of WO_6 octahedra (Figure 1) and is completely shielded from contact with external species.[10] The WO_6 shell is stable under even rather strenuous conditions,[7,11-13] and hence the Co(III) ion in $Co^{III}W$ is as effectively caged as in $[Co(sepulchrate)]^{3+}$, a member of another class of caged ions that has attracted interest recently.[14] $Co^{III}W$ has however a much higher $E°$ value, 1.0 V vs. NHE[13] compared to −0.3 V for sepulchrate, and is therefore a much stronger oxidant. In kinetic studies, $Co^{III}W$ is expected to behave as a one-electron oxidant toward aromatics that are not too easily oxidized (the second reduction step, involving transfer of two electrons to the WO_6 shell has an $E°$ around −0.5 V[15]), and it should be free from the complexities of other Co(III) species, e.g., cobalt(III) acetate, with respect to oligomerization and ligand exchange.[16] An additional advantage of using $Co^{III}W$ as a model compound for electron transfer oxidation is the extremely low ability to form solvates via hydrogen bonding,[17] thus minimizing the usual strong inhibition of electron transfer through solvation and, especially, hydration shells.[4]

This paper reports results of a detailed kinetic study of the reaction between $Co^{III}W$ and *p*-methoxytoluene in 55/45 (w/w) acetic acid/water. The system was selected because of the relatively well-explored electron-transfer properties of *p*-methoxytoluene (PMT)[5a,b,6a,18,19] and the necessity of keeping the dielectric

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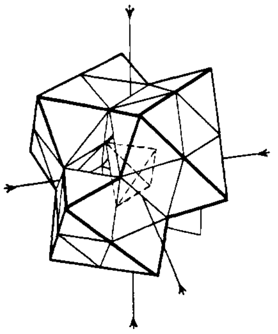

Figure 1. Structure of the 12-tungstocobalt(III)ate ion (the Keggin structure). The Co(III) ion is situated in the center of the tetrahedron, and the tungsten atoms are situated in the octahedron centers. Each corner of an octahedron represents an oxygen atom.

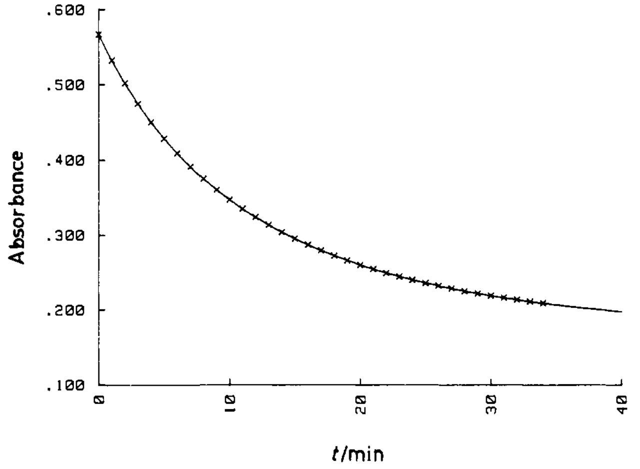

Figure 2. Diagrammatic representation of a kinetic run. The crosses correspond to the experimental points, and the curve corresponds to the best possible fit to the data according to eq 8: $P(1) = 0.182$ (2); $P(2) = 0.0581$ (2); $P(3) = 0.377$ (4); sum of standardized square residuals = 1.1×10^{-6}.

constant of the medium as high as possible to avoid complications due to excessive ion pairing. The kinetic data are in agreement with a mechanism involving an initial reversible electron-transfer step, followed by a rate-determining proton-transfer step. Estimates of electron-transfer rate constants using the Marcus theory are in accordance with results from this study.

Results

Stoichiometry. Our exploratory study[7a] of the oxidation of methyl aromatic compounds (toluene, *o*- and *p*-xylene, mesitylene, hexamethylbenzene, and PMT) by $Co^{III}W$ in acetic acid media established the overall two-electron oxidative properties of this reagent.[8] Thus, the major product in all cases is the α acetoxy derivative, accompanied by lesser amounts of the alcohol when water is present. Also the nuclear acetate was detected in favorable cases (mesitylene). As a minor side reaction, the structural element of CH_2OAc was also introduced into the nucleus of difficulty oxidizable substrates, presumably via attack by $HOOCH_2\cdot$ to give the arylacetic acid, followed by its oxidative decarboxylation.[7c] In the particular case of PMT, a dehydro dimer (2-(4-methoxybenzyl)-4-methylanisole) was formed as a minor product in the absence of any added acetate salt; this product was greatly reduced (from 21 to 0.6%) in the presence of 0.1 M KOAc.

Thus, the overall redox behavior of $Co^{III}W$ toward methyl aromatics is to produce the range of two-electron oxidation products usually found for high-valent metal ions.[5-7] Since the reaction conditions under which the above-mentioned study was performed (100 °C; substrate to $Co^{III}W$ molar ratio 5:1; lower water and KOAc concentrations) were different from those prevailing during the kinetic experiments described here, a product study was carried out for PMT for a more representative set of reaction conditions (50 °C, substrate to $Co^{III}W$ ratio 50:1; 55/45 (w/w) $HOAc/H_2O$; [KOAc] = 0.5 M). This study gave 35.5 and 47% of the α acetate and α alcohol, respectively. As expected in view of the high acetate ion concentration, no dimer was detectable (i.e., less than 0.2% yield).

Kinetic Method and Data Treatment. The reaction was followed at 50.0 °C by monitoring the absorbance of $Co^{III}W$ at 390 nm in the presence of a large excess of PMT (concentration ratio generally ca. 1:100). Attempts to treat absorbance/time data according to a simple first-order kinetic model failed, and the kinetic model represented by eq 1 and 2 was eventually found to give a good fit to the data. In eq 1 and 2 A represents $Co^{III}W$, B PMT, C $PMT^{+}\cdot$, D $Co^{II}W$, E a base (generally acetate ion), and P products, with $[A] \ll [B]$ and $[E] \gg [C]$. Using the steady-state approximation on [C], one eventually obtains eq 3 in which k' and c are given by eq 4 and 5, respectively, [B] and [E] being essentially constant during a run.

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D \tag{1}$$

$$C + E \xrightarrow{k_2} P \tag{2}$$

$$-d[A]/dt = k'[A]/(c + [D]) \tag{3}$$

$$k' = (k_1k_2/k_{-1})[B][E] \tag{4}$$

$$c = (k_2/k_{-1})[E] \tag{5}$$

Introducing $[D] = [A]_0 - [A]$ into (3), followed by separation of variables and integration, gives eq 6. Replacement of $[A]_0$

$$k't = (c + a)\ln([A]_0/[A]) + ([A] - [A]_0) \tag{6}$$

by a and [A] by $(a - x)$ gives the possibility of entering the usual expression for a, $(a - x)$, and x in terms of absorbance values (f's in eq 7, in which b is a proportionality constant). In order to obtain

$$k't = (c + a)\ln\frac{f_0 - f_\infty}{f - f_\infty} - [b(f_0 - f)] \tag{7}$$

an explicit expression for f as a function of t, it is necessary to use the approximation $\exp(bf/(c + a)) \approx 1 + bf/(c + a)$ (see below), after which expression 8 can be derived. In (8) $P(2)$ is the kinetic parameter of interest and is given by eq 9, where $[A]_0$

$$f = \frac{f_\infty + P(1)\exp[-P(2)t]}{1 - P(3)\exp[-P(2)t]} \tag{8}$$

$$P(2) = \frac{k_1k_2[B][E]}{k_{-1}[A]_0 + k_2[E]} \tag{9}$$

equally well can be replaced by $[D]_\infty$ (the term $k_{-1}[A]_0 = k_{-1}[D]_\infty$ accounts for the back-electron-transfer reaction). $P(1)$–$P(3)$ are evaluated by fitting the f/t data to expression 8 by a nonlinear regression method.

In order to treat the kinetic data according to (8), it is first necessary to establish that the approximation made above is valid. From the UV spectrum of $Co^{III}W$ and the concentration levels employed, it is evident that $b/(c + a)$ always is less than 1, and then it would seem possible to obtain good values of $P(2)$ provided the f values are kept below a certain level. This assumption was shown to be valid by collecting 200 f/t observations, beginning at as high an f value as possible and computing $P(2)$ after successive removal of 0, 10, 20, etc. observations starting at the beginning of the reaction period. As can be seen from the two runs exemplified in Table I, $P(2)$ is effectively constant at f values

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Table I. Calculation of $P(2)$ after Omitting Data during Initial Periods of Different Duration

run no.	no. of observns	$f_{\max}$ during period	$P(2)$/min^{-1}	squared residual sum
1	200	0.9363	0.0501 (12)	2×10^{-3}
	190	0.7452	0.0543 (3)	1.5×10^{-4}
	180	0.6349	0.0556 (2)	2.8×10^{-5}
	170	0.5596	0.0559 (3)	2.2×10^{-5}
	160	0.4999	0.0561 (2)	1.9×10^{-5}
	150	0.4540	0.0562 (2)	1.8×10^{-5}
	140	0.4162	0.0561 (1)	1.7×10^{-5}
2	200	0.9418	0.0104 (3)	1.8×10^{-3}
	190	0.6949	0.0116 (1)	1.7×10^{-4}
	180	0.5696	0.0120 (1)	4.7×10^{-5}
	170	0.4881	0.0123 (1)	2.2×10^{-5}
	160	0.4244	0.0122 (1)	1.1×10^{-5}

Table II. Effect of Varying [PMT], [KOAc], and $[\mathrm{Co^{III}W}]_0$ upon $P(2)$ in 55/45 (w/w) HOAc/H_2O at 50.0 °C

[PMT]/M	[KOAc]/M	$[\mathrm{Co^{III}W}]_0$/mM	$P(2)$/min^{-1}
0.047	0.47	0.94	0.028
0.059	0.47	0.94	0.034
0.070	0.47	0.94	0.043
0.082	0.47	0.94	0.050
0.094	0.47	0.94	0.059
0.105	0.47	0.94	0.068
0.117	0.47	0.94	0.071
0.129	0.47	0.94	0.079
0.141	0.47	0.94	0.085
0.094	0.038	0.94	0.0028
0.094	0.056	0.94	0.0031
0.094	0.075	0.94	0.0045
0.094	0.094	0.94	0.0060
0.094	0.113	0.94	0.0069
0.094	0.131	0.94	0.0081
0.094	0.150	0.94	0.0096
0.094	0.169	0.94	0.0118
0.094	0.188	0.94	0.0135
0.094	0.211	0.94	0.0159
0.094	0.234	0.94	0.0175
0.094	0.70	0.94	0.109
0.094	0.94	0.94	0.174
0.094	1.17	0.94	0.257
0.094	1.41	0.94	0.340
0.094	1.64	0.94	0.407
0.094	1.88	0.94	0.542
0.094	0.47	0.248	0.174
0.094	0.47	0.297	0.146
0.094	0.47	0.355	0.119
0.094	0.47	0.489	0.099
0.094	0.47	0.72	0.076
0.094	0.47	1.78	0.033
0.094	0.47	1.78[a]	0.031
0.094	0.47	2.52[a]	0.023
0.094	0.47	3.19[a]	0.020

[a] The reaction was run with $\mathrm{Co^{II}W}$ present initially and with $\mathrm{Co^{III}W}$ added in an amount corresponding to $[\mathrm{Co^{III}W}]_0$ of ca. 1 mM.

below 0.6. Hence calculations of $P(2)$ were based on data (normally 30–80 observations) following the first half-life period of the reaction. Figure 2 illustrates the excellent fit of the experimental data to the model.

All rate constants given in Table II–VI are mean values from at least five runs. The reproducibility is generally good, to ±3–5% in most cases. Exceptions are runs in media of very low [AcO^-] where catalysis by acid liberated during the run causes larger deviations. Since most rate constants refer to well-buffered media, this source of error is not serious.

Concentration Dependence of P(2). Figure 3 shows the dependence of log $P(2)$ on log [PMT] (for data, see Table II). The slope of the line is 1.03 (6), in good agreement with eq 9. Figure 4 demonstrates the linear relation between log $P(2)$ and log [AcO^-] (for data, see Table II), the slope being 1.1 (1) in the interval between 0.04 and 0.25 M [AcO^-] and 1.6 (1) between 0.5 and

Table III. Specific-Cation Effect on the Rate of Oxidation of PMT by $\mathrm{Co^{III}W}$[a]

	rate constant			
	$P(2)^b$/min^{-1}		$P(2)^c$/min^{-1}	
cation (M)	abs	rel	abs	rel
Li^+	0.0323	1.11	0.0337	1.16
Na^+	0.0291	1.00	0.0291	1.00
K^+	0.0332	1.12	0.0591	2.03
Rb^+	0.0339	1.16		
Cs^+	0.0413	1.42	0.173	5.95
Ca^{2+}	0.0368	1.26		
Sr^{2+}	0.0432	1.48		
Me_4N^+	0.0196	0.67		
Et_4N^+	precipitation occurs			
Pr_4N^+	0.00724	0.25		
Bu_4N^+	0.00821	0.28	5×10^{-5}	1.7×10^{-3}
Hex_4N^+	0.0202[d]			
Dec_4N^+	0.0114[e]			
$PyCH_3^+$	0.0138	0.47		

[a] $[\mathrm{Co^{III}W}]_0 = 9.4 \times 10^{-4}$ M; [PMT] = 0.094 M; medium 55/45 (w/w) acetic acid/water; temperature 50.0 °C. [b] [$MClO_4$] = 4.7×10^{-2} M; [NaOAc] = 0.47 M. [c] [MOAc] = 0.47 M. [d] [Hex_4NClO_4] = 9.4×10^{-3} M. [e] Saturated with Dec_4NClO_4 at 50.0 °C (1-2 mM).

Table IV. Effect of Varying [Bu_4NX] upon $P(2)$ in 55/45 (w/w) HOAc/H_2O at 50.0 °C[a]

	$P(2)$/min^{-1}	
$Bu_4N^+X^-$	$X^- = BF_4^-$	$X^- = ClO_4^-$
0	0.029	
0.0234	0.0157	
0.047	0.0080	0.0082
0.070	0.0055	
0.094	0.0032	0.0041
0.117	0.0021	
0.141	0.00147	
0.188	[b]	0.00142

[a] [PMT] = 0.094 M; [NaOAc] = 0.47 M; $[\mathrm{Co^{III}W}]_0$ = 0.94 mM. [b] Solubility not high enough.

Table V. Effect of Varying the Solvent Composition upon $P(2)$[a]

HOAc/% (w/w)	D^b	$P(2)$/min^{-1}
50	55.4	0.080
55	51.2	0.059
60	46.8	0.041
65	42.2	0.030
70	37.4	0.023

[a] [PMT] = 0.094 M; [KOAc] = 0.47 M; $[\mathrm{Co^{III}W}]_0$ = 0.94 M; 50.0 °C. [b] Extrapolated by means of a quadratic equation based upon data in ref 20.

Table VI. Deuterium Isotope Effects in the Oxidation of PMT by $\mathrm{Co^{III}W}$[a]

ratio HOAc/H_2O (w/w) in solv	added salt(s) (concn/M)	temp/°C	$P(2)_H$/$P(2)_D$	ref
55/45	KOAc (0.094)	50.0	5.0 (5)	this work
55/45	KOAc (0.188)	50.0	4.5 (5)	this work
55/45	KOAc (0.47)	50.0	5.4 (5)	this work
55/45	KOAc (1.88)	50.0	4.7 (5)	this work
55/45	none	50.0	7.3 (7)	this work
50/50	KOAc (0.47)	102	5.4 (5)	this work
75/25	none	102	6.0 (2)[b]	7a
75/25	KOAc (0.1)		5.6 (2)[b]	7a

[a] [PMT-α,α,α-d_3] or [PMT] = 0.094 M; $[\mathrm{Co^{III}W}]_0 = 9.4 \times 10^{-4}$ M. [b] Determined by competition experiments between PMT and PMT-α,α,α-d_3.

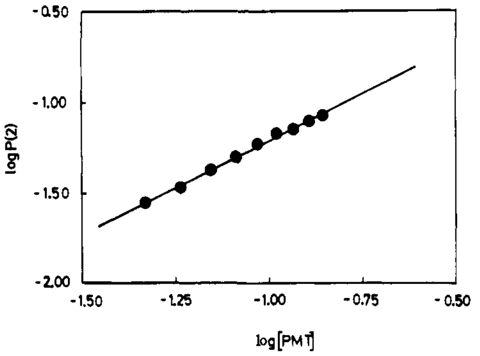

Figure 3. Plot of log ($P(2)$) vs. log [PMT] (see Table II).

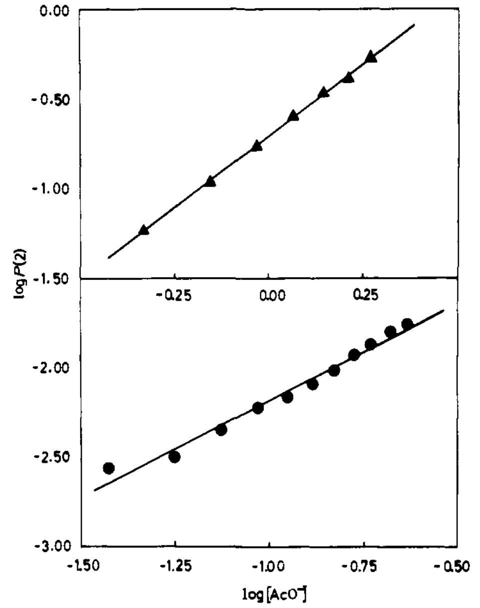

Figure 4. Plot of log ($P(2)$) vs. log [KOAc]: circles, 0.04–0.25 M; triangles, 0.5–2 M (see Table II).

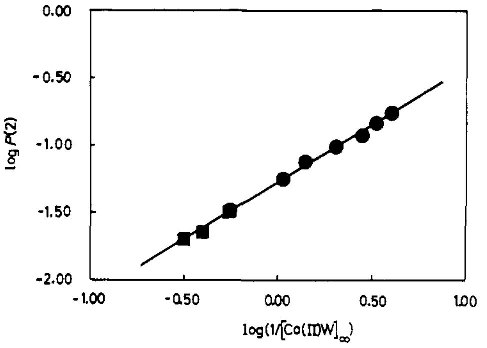

Figure 5. Plot of log ($P(2)$) vs. log ($1/[\mathrm{Co^{II}W}]_\infty$) (see Table II). Circles correspond to runs where all heteropolyions are added intially and squares to runs where a certain concentration of Co(II)W was initially present in the solution.

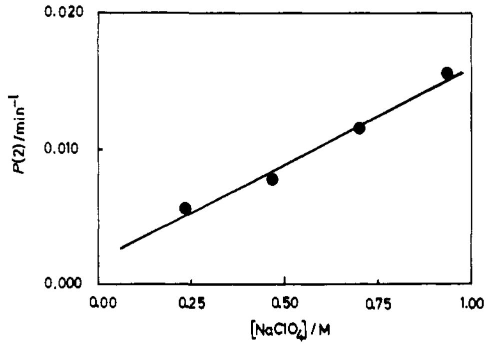

Figure 6. Plot of $P(2)$ vs. [$NaClO_4$]. The slope of the line is 0.014 M^{-1} min^{-1} and the intercept on the y axis 0.0018 min^{-1}.

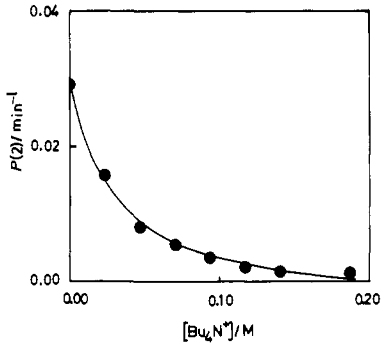

Figure 7. Plot of $P(2)$ vs. [Bu_4N^+] (see Table IV).

2.0 M. Finally, a linear plot of log $P(2)$ vs. log ($1/[\mathrm{Co^{II}W}]_\infty$) is shown in Figure 5 (for data, see Table II), the slope being 0.85 (5). In the last-mentioned case the reactions were run in two complementary ways, namely either by adding Co^{III}W to the kinetic sample to produce the initial concentration given in the column head of Table II (at low concentrations of Co^{III}W) or by having a certain concentration of Co^{II}W present from the beginning and adding Co^{III}W in an amount corresponding to an initial concentration of ca. 1 mM (at higher total concentrations of heteropolyion). In the case where both modes were employed, the rate constants agreed within the limits of experimental errors.

The experimental reaction orders are thus in reasonable agreement with eq 9, provided it can be assumed that the k_2[E] term in the denominator is negligible with respect to $k_{-1}[A]_0$. As shown in the discussion below, this requirement is a logical consequence of the exergonicity of the k_{-1} step ($E°$ of PMT is 1.82 V vs. 1.00 V for Co^{III}W).

Specific-Ion Effects. The effect of the an inert salt, sodium perchlorate, upon $P(2)$ is shown by Figure 6. This salt was chosen since potassium perchlorate is too insoluble in the medium employed to allow for salt-effect studies. In the course of these experiments a strong influence on rate by the nature of the cation was noticed, and therefore the study was extended to elucidate this effect in detail. Table III lists such data for a large number of ions, and it is especially noteworthy that tetraalkylammonium ions have a strong inhibiting effect on the reaction, the larger ions being more effective in this respect. Thus tetradecylammonium ion gives a more pronounced rate retardation at the 1–2 mM level than tetramethylammonium ion does at a concentration of ca. 0.05 M.

Tetrabutylammonium ion was singled out for a closer investigation of the concentration dependence of this special ion effect (Figure 7 and Table IV) and showed the expected saturation phenomenon at higher concentrations.

The addition of a crown ether, 18-crown-6, to the potassium acetate catalyzed reaction had a similar inhibiting effect as a tetraalkylammonium ion, although not as strong. Thus, 0.25 M 18-crown-6 decreased $P(2)$ in 55/45 $HOAc/H_2O$, 0.47 M in potassium acetate, by a factor of ca. 10, whereas tetrabutylammonium ion under the same conditions produced a 100-fold rate retardation.

Finally, it was established that the reaction is catalyzed by acid, $P(2)$ being 0.035 (1) min^{-1} in the presence of 0.1 M methanesulfonic acid or ca. 100 times larger than the value in the neat solvent.

Solvent Effect. The effect of changing composition of the solvent was studied in the range of 50–70% acetic acid/water with [KOAc] = 0.47 M and [PMT] = 0.094 M. The results are displayed in Figure 8 (for data, see Table V), where log $P(2)$ is plotted vs. $1/D$ (D is the dielectric constant of the medium).

Isotope Effects. As already shown by competition experiments,[7a] the oxidation of PMT by Co^{III}W shows an appreciable primary kinetic deuterium isotope effect. Table VI lists kinetically determined values of k_H/k_D under different conditions.

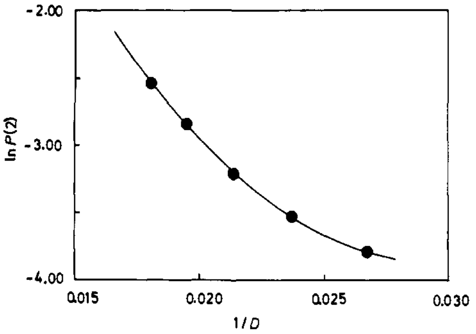

Figure 8. Plot of ln ($P(2)$) vs. $1/D$ (see Table V).

Cyclic Voltammetry. The electrochemical behavior of $Co^{III}W$ has been well explored,[13,15] and here it was only necessary to study the effect of medium and electrolyte in order to make sure that no abnormal effects from these factors appear. Thus cyclic voltammetry of the $Co^{III}W/Co^{II}W$ couple in 55/45 (w/w) $HOAc/H_2O$ with 0.47 M KOAc or Bu_4NOAc present (Pt electrode, sweep rate 0.1 V s^{-1}) showed that reversibility is preserved in these media, the $[((E_p)_c + (E_p)_a)/2]$ values being 1.01 and 0.76 V, respectively. The $E°$ value of $Co^{III}W/Co^{II}W$ in water is 1.01 V,[13] so the KOAc system is not different from water in this respect. On the other hand, the presence of tetrabutylammonium ion causes a rather pronounced decrease in the oxidation potential (see Discussion).

Discussion

In order to discuss the data reported above, we need estimates of k_1 and k_{-1} in addition to knowledge about the behavior of electron-transfer processes with respect to changes in dielectric constant, ionic strength, nature of added cations, etc. Rate constants for electron transfer are normally calculated within the framework of the Marcus theory,[4,22] which treats the reactants as two spheres immersed in a continuous medium of dielectric constant D with a distance between the reacting centers in the encounter complex/transition state of r_{12} (here expressed in angstroms). In order to reach the transition state from the encounter complex, the two components undergo bond reorganization, coupled with solvent reorganization with a reorganization energy of λ (kcal mol^{-1}). In the situation where the energy levels between which the electron is transferred match each other exactly, the transition state has been reached and the electron can be transferred without any nuclear movements (the Franck–Condon principle).

The Marcus theory is valid for inorganic[21] as well as organic[4] outer-sphere (for organic ones, the term "nonbonded" is perhaps more appropriate)[3f,g] electron-transfer processes, i.e., where the electronic coupling between the two reactants in the transition state is negligible (≤1 kcal mol^{-1}). The rate constant (k_{el}) of a nonbonded electron-transfer reaction can then be estimated from the Eyring equation (eq 10a) and the Marcus expression for ΔG_{el}^{*}

$$k_{el} = 10^{11} \exp(-\Delta G_{el}^{*}/RT) \tag{10a}$$

$$\Delta G_{el}^{*} = W + (\lambda/4)(1 + \Delta G°'/\lambda)^2 \tag{10b}$$

(eq 10b). Here W is the electrostatic work expended to bring the two reactants together, and $\Delta G°'$ is the free energy change of the reaction, corrected by a term involving the gain or loss of electrostatic energy upon transfer of an electron within the transition state. The latter term is of course important for the highly charged ions treated in this investigation. For reaction between $Co^{III}W^{5-}$ and a neutral organic molecule, the transfer of an electron in the transition state leads to an appreciable gain in electrostatic stabilization, Z_1Z_2 changing from 0 to -6 (Z_1 and Z_2 are the ionic charges of the reactants).

Equations 10a and 10b provide a method for estimating the two electron-transfer rate constants k_1 and k_{-1} of eq 1. Since one of the reactants is neutral, W can be neglected. The λ value of the self-exchange reaction between $Co^{III}W$ and $Co^{II}W$ (eq 11)

$$Co^{III}W^{5-} + Co^{II}W^{6-} \rightleftharpoons Co^{II}W^{6-} + Co^{III}W^{5-} \tag{11}$$

has been experimentally determined[11] at 0 °C from the self-exchange rate constants of 0.03 and 0.54 M^{-1} s^{-1} at ionic strength (μ) of 0.015 and 0.5, respectively, and is 63 and 56 kcal mol^{-1}. Extrapolation of the rate data given by Rasmussen and Brubaker[11] to 50 °C gives $\lambda(Co^{III}W/Co^{II}W)$ of 64 kcal mol^{-1} in both cases. It is however necessary to correct this λ value for the electrostatic work (W_1) involved in bringing $Co^{III}W^{5-}$ and $Co^{II}W^{6-}$ together (eq 11) in the self-exchange reaction in order to obtain what Pellizzetti et al. have termed its "intrinsic" value.[22] This is done by eq 12 where all parameters have been defined in the text above.

$$W_1 = \frac{(1.33 \times 10^3)Z_1Z_2}{Dr_{12}} 10^{-(21.9r_{12}(\mu/DT)^{1/2})} \tag{12}$$

With D equal to 51.2 for 55/45 (w/w) $HOAc/H_2O$ and r_{12} taken to be 10 Å, W_1 is calculated to be 48 and 4.9 kcal mol^{-1} for μ = 0.015 and 0.5, respectively. Now it is well-known that eq 12 overcorrects for high ionic strengths, and hence the "averaged" method by Haim and Sutin[22b] was employed to give W_1 = 41 kcal mol^{-1} at μ = 0.5, and thus the intrinsic λ values at μ = 0.015 and 0.5 are (64 – 48) = 16 and (64 – 41) = 23 kcal mol^{-1}, respectively.

The λ value for self-exchange between PMT and $PMT^{+}\cdot$ is not known, but in view of the constancy of λ for self-exchange reactions of a large number of aromatic compounds in the region of 8–10 kcal mol^{-1}, a value of 9.0 kcal mol^{-1} can safely be used.[4] Thus the Marcus theory gives λ of eq 1 as $^1/_2(16 + 9)$ = 12.5 kcal mol^{-1} at μ = 0.015 and $^1/_2(23 + 9)$ = 16 kcal mol^{-1} at μ = 0.5.

$\Delta G°'$ for eq 1 was obtained from $E°$ values of $Co^{III}W$ (1.01 V vs. NHE under the conditions employed here; Simmons[13] gave 1.00 V at infinite dilution in water) and PMT (1.82 V in acetonitrile,[23] in the medium used here, it is probably slightly lower), corrected by an electrostatic term according to eq 12, with r_{12} = 7 Å and D = 51.2. Again the "averaged" method by Haim and Sutin[22b] was used for estimating W_1 at high ionic strength. The results are shown in Table VII where the values in the first two rows refer to the data given in the text and the remaining ones are included to demonstrate the effect of variations in $\Delta G°'$ and λ. These variations were chosen so as to represent possible extremes of these parameters.

It can first be concluded that no reasonable variation in $\Delta G°'$ and/or λ changes k_{-1} from its diffusion-controlled value. Thus we can be sure that the $k_2[E]$ term in the denominator of eq 9 can be neglected under all circumstances with respect to k_{-1} $[A]_0$ $\approx 10^7$ s^{-1}, in agreement with the reaction orders experimentally found. From this starting point k_2 can be calculated from $P(2)$ at μ = 0.015, the ionic strength of a solution where [KOAc] = 0 and $[Co^{III}W]$ = 1.00 mM. The rate constant for this situation was estimated by linear extrapolation of the $k/[AcO^-]$ data pairs in the region between 0.038 and 0.113 M $[AcO^-]$ to 0 M $[AcO^-]$ and was 0.00023 min^{-1}. In this case water (25 M) must be the species predominantly responsible for proton abstraction from $PMT^{+}\cdot$, and at μ = 0.5 the acetate ion (0.5 M) acts as the base in eq 2. These k_2 values come out as 80 and 3.6 × 10^6 M^{-1} s^{-1}, respectively.

The rate constants for proton abstraction from $PMT^{+}\cdot$ by different basic species are unfortunately not known, but those for proton abstraction from methyl aromatic hydrocarbon radical cations by water typically fall in the range between 10^2 and 3 × 10^5 M^{-1} s^{-1} (tri-, tetra-, penta-, and hexamethylbenzenes).[24] The k_{AcO^-}/k_{H_2O} ratio for 1,2,3,5-tetramethylbenzene is also known and is ca. 2000. Thus the k_2 values estimated for proton abstraction

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[22] (a) Pelizzetti, E.; Mentasti, E.; Pramauro, E. *Inorg. Chem.* **1978**, *17*, 1688. (b) Haim, A.; Sutin, N. *Ibid.* **1976**, *15*, 476.

[23] Eberson, L.; Jönsson, L.; Wistrand, L.-G. *Acta Chem. Scand., Ser. B* **1978**, *B32*, 520.

[24] A compilation of rate constants for proton abstraction from alkylaromatic compounds is given in ref 26. See also: (a) Sehestad, K.; Holcman, J. *J. Phys. Chem.* **1978**, *82*, 651. (b) Parker, V. D. *Acta Chem. Scand., Ser. B* **1981**, *B35*, 123. (c) Barek, J.; Ahlberg, E.; Parker, V. D. *Ibid.* **1980**, *B34*, 85.

Table VII. Estimates of k_{el} (M^{-1} s^{-1}) According to Eq 10a,b[a]

		λ/kcal mol⁻¹					
		12.5		16		20	
ionic strength	$\Delta G^{\circ b}$/ kcal mol⁻¹	k_1	$k_{-1}/10^{10}$	k_1	$k_{-1}/10^{10}$	k_1	$k_{-1}/10^{10}$
0.015	14.7	10.6	8.4	11.7	9.6	6.9	5.7
0.50	15.5	2.5	7.6	3.3	9.4	2.2	6.7
	10	1.4×10^4	8.2	7.2×10^3	4.2	2.5×10^3	1.43
	11	3.4×10^3	9.3	2.0×10^3	5.4	7.5×10^2	2.1
	12	7.6×10^2	9.9	5.2×10^2	6.8	2.2×10^2	2.9
	13	1.6×10^2	9.9	1.3×10^2	8.0	62	3.9
	14	32	9.3	31	9.1	17	5.0
	15	5.9	8.2	7	9.8	4.4	6.1
	16	1.0	6.8	1.5	10	1.1	7.3
	17	0.17	5.3	0.31	9.8	0.27	8.4
	18	2.6×10^{-2}	3.9	6×10^{-2}	9.1	6.2×10^{-3}	9.3
	19	3.8×10^{-3}	2.7	1.1×10^{-2}	8.0	1.1×10^{-2}	9.8
	20	5.2×10^{-4}	1.7	2×10^{-3}	6.8	3×10^{-3}	10

[a] For the choice of parameter values, see text. [b] Absolute value; k_1 corresponds to a positive value and k_{-1} to a negative one.

from $PMT^{+}\cdot$ are well compatible with known data from similar processes.

As seen from Table VII, the Marcus treatment predicts a slight decrease in k_1 with increasing ionic strength for the $Co^{III}W$/PMT reaction. Since we actually observe the opposite behavior of $P(2)$ (Figure 6), this effect must either operate on eq 2; i.e., k_2 should be subject to a positive salt effect due to increasing ionic strength or be a reflection of the specific-cation effect demonstrated in Tables III and IV and Figure 7. In view of the high ionic strengths employed it is difficult to distinguish between these alternatives. Although at low ionic strength ($\mu \leq 0.01$) the Debye–Hückel theory predicts that a reaction involving a singly charged species and a neutral molecule [eq 2, B = H_2O] should not exhibit any salt effect at all, it is known that neutral species are affected by high ionic strength with either rate acceleration or rate retardation as the result.[25]

In view of the pronounced specific-cation effect on the reaction rate (Tables III and IV and Figure 7), it is, however, most likely that this factor is the most important one and in fact must have a deciding influence on the theoretical treatment of the process. We have, for example, calculated the electrostatic terms above from the formal charges of $Co^{III}W^{5-}$ and $Co^{II}W^{6-}$, which obviously is an extreme case. It is more realistic to assume that ion pairs like $[Co^{III}W,M^{+}]^{4-}$, $[Co^{III}W,M_2^{2+}]^{3-}$, etc. are the kinetically active species. There is indeed considerable evidence[21d] for association between cations and multicharged anions, e.g., in the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ system. For the self-exchange process $Fe(CN)_6^{3-/4-}$ the catalytic/inhibitory effect of cations upon rate constants has been studied in detail,[26a,b] and Figure 9 shows a logarithmic plot of relative rate constants [$P(2)$] in the $Co^{III}W$/PMT reaction and the $Fe(CN)_6^{3-/4-}$ self-exchange process.[26a,b] It should be noted that the rate constants of the latter reaction have been determined in two investigations under rather different conditions and the corrections applied here refer only to temperature effects. Thus the correlations, although seemingly good, should only be considered to be semiquantitatively valid.

In principle, the treatment shown in Figure 9 can be objected against because the data for the $Fe(CN)_6^{3-/4-}$ system reflect kinetic behavior, whereas P(2) is influenced (eq 9) by both the thermodynamics of the electron-transfer step (k_1/k_{-1}) and the kinetics of proton abstraction (k_2). However, in view of the fact that calculated k_{-1} values (see Table VII) vary by a factor of 7 only over a range of $\Delta G^{\circ\prime}$ = 10 kcal mol⁻¹ and λ = 7.5 kcal mol⁻¹, it is largely k_1k_2 that influences $P(2)$. With the assumption that the base activity is independent of the nature of the cation at one and the same concentration level, the rate constant of the forward electron-transfer reaction (k_1) would be the parameter that is predominantly influenced by the cation effect. The uncertainties of this assumption should be kept in mind in all discussions of $P(2)$.

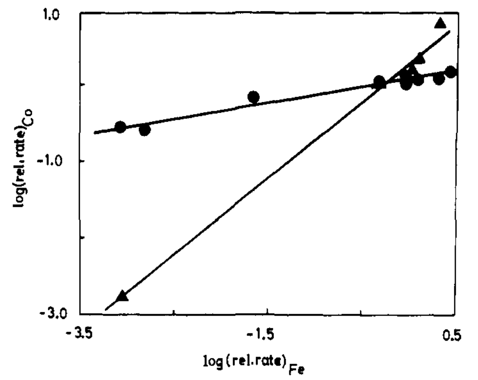

Figure 9. Plot of log ($k_{rel}(Co^{III}W)$) vs. log ($k_{rel}(Fe(CN)_6^{3-/4-})$) with respect to different cations (see Table III). The line with the greater slope corresponds to the data in column 5.

Attempts to analyze quantitatively the kinetic consequences of ion-pair formation, as shown in Figure 7, in terms of the simple reaction scheme given in eq 13–15 failed, since the kinetic data

$$P(2) = k'[(Co^{III}W)^{5-}] + k''[(Na^{+}Co^{III}W)^{4-}] + k'''[(Bu_4N^{+}Co^{III}W)^{4-}] \quad (13)$$

$$Na^{+} + (Co^{III}W)^{5-} \overset{K_1}{\rightleftharpoons} (Na^{+}Co^{III}W)^{4-} \quad (14)$$

$$Bu_4N^{+} + (Co^{III}W)^{5-} \overset{K_2}{\rightleftharpoons} (Bu_4N^{+}Co^{III}W)^{4-} \quad (15)$$

are not sufficient to evaluate all five parameters of the scheme. Moreover, the approximations necessary to obtain a manageable expression for the mathematical analysis probably were not in the allowed range. Semiquantitatively, values of K_1 and K_2 appear to be of the order of 10^1 and 10^3, respectively.

Several explanations or combinations thereof can be given for the specific-cation effect. In the $Fe(CN_6)^{3-/4-}$ case it is known that E° values decrease from Cs^{+} to Li^{+} and that tetraalkylammonium ions decrease E° still more.[27] For $Co^{III}W^{5-/6-}$ we have measured an E° decrease of 0.25 V in going from 0.5 M

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(25) Frost, A.; Pearson, R. G. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961; pp 150–153.

(26) (a) Shporer, M., Ron, G., Loewenstein, A.; Navon, G. *Inorg. Chem.* **1965**, *4*, 361. (b) Campion, R. J.; Deck, C. F.; King, P. Jr.; Wahl, C. *Ibid.* **1967**, *6*, 672. (c) Recently, a catalytic effect of all types of cations has been observed in the reactions between hexachloroiridate(IV) ion and different anionic metal complexes: Bruhn, H.; Nigam, S.; Holzwarth, J. F. *Faraday Discuss. Soc.*, in press.

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(32) Jönsson, L.; Wistrand, L.-G. *J. Chem. Soc., Perkin Trans. 1* **1979**, 669.

Table VIII. Primary Kinetic Isotope Effects in the Oxidation of Alkyl Aromatic Compounds by Established or Suspected Electron-Transfer Reagents

oxidant	radical cation[a]	base/solvent (temp/°C)	k_H/k_D	ref
anode	$(\mathrm{PhEt})^{+\cdot}$	$\mathrm{AcO^-/AcOH}$ (25)	2.6	5b
anode	$(\mathrm{C_6Me_6})^{+\cdot}$	$\mathrm{CH_3CN/CH_3CN}$ (22)	4.8	24b
anode	$(1,2,3\text{-}\mathrm{Me_3}\text{-}5\text{-}t\text{-}\mathrm{BuC_6H_2})^{+\cdot}$ [b]	AcOH/AcOH (60)	7.2	28
anode	$(1,2,3\text{-}\mathrm{Me_3}\text{-}5\text{-}t\text{-}\mathrm{BuC_6H_2})^{+\cdot}$ [b]	$\mathrm{AcO^-/AcOH}$ (60)	1.8	28
Ce(IV)[c]	$(1,2,3\text{-}\mathrm{Me_3}\text{-}5\text{-}t\text{-}\mathrm{BuC_6H_2})^{+\cdot}$ [b]	AcOH/AcOH (60)	3.2	28
Ce(IV)[c]	$(\mathrm{C_6Me_6})^{+\cdot}$	AcOH/AcOH (25)	5.4	6a
Ce(IV)[c]	$(\mathrm{PMT})^{+\cdot}$	AcOH/AcOH (25)	6.2	6a
Ce(IV)[c]	$(1,4\text{-}\mathrm{Me_2C_6H_4})^{+\cdot}$	$\mathrm{CH_3CN/CH_3CN}$ (84)	2.3	6c
Co(III)[d]	$(1,2,3\text{-}\mathrm{Me_3}\text{-}5\text{-}t\text{-}\mathrm{BuC_6H_2})^{+\cdot}$ [b]	AcOH/AcOH (60)	6.7	28
Co(III)[d]	$(\mathrm{PhMe})^{+\cdot}$	$\mathrm{AcO^-/AcOH}$ (24)	3.7	29
Co(III)[e]	$(\mathrm{PhMe})^{+\cdot}$	$\mathrm{CF_3COO^-/CF_3COOH\text{-}AcOH}$ (20)	1.1	30
Mn(III)[f]	$(\mathrm{PMT})^{+\cdot}$	AcOH/AcOH (70)	5.1	5a
Ag(II)[g]	$(\mathrm{PMT})^{+\cdot}$	$\mathrm{AcO^-/AcOH}$ (25)	5.9	18
Cu(III)[h]	$(1,4\text{-}\mathrm{Me_2C_6H_4})^{+\cdot}$	$\mathrm{CF_3COO^-/CF_3COOH\text{-}AcOH}$ (100)	2.5	31
$\mathrm{SO_4}^{-\cdot}$ [i]	$(\mathrm{PhMe})^{+\cdot}$	$\mathrm{AcO^-/AcOH}$ (110)	2.2	32

[a] With the appropriate deuterium substitution. [b] For substitution in the 2-methyl group. [c] As $[\mathrm{Ce(NO_3)_6}]^{2-}$. [d] $\mathrm{Co(OAc)_3}$. [e] $\mathrm{Co(CF_3COO)_3}$. [f] $\mathrm{Mn(OAc)_3}$. [g] $[\mathrm{Ag(bpy)_2}]^{2+}$. [h] $[\mathrm{bis(biuretato)Cu^{III}}]^-$. [i] By thermal decomposition of $\mathrm{S_2O_8}^{2-}$.

KOAc to 0.5 M $\mathrm{Bu_4NOAc}$, corresponding to a calculated k_1 change according to eq 10a,b from 2.5 to 7.5×10^{-5} $\mathrm{M^{-1}\,s^{-1}}$ for $\lambda = 12.5$ kcal mol^{-1} or a factor of 3×10^{-5} (observed 8×10^{-4}, see Table III). For $\lambda = 16$ and 20 kcal mol^{-1} the factor is ca. 10^{-4} and 8×10^{-4}, respectively. The explanations forwarded[21b,26a,b] assume either that the cation has a catalytic/inhibitory effect in the ion pair by facilitating/inhibiting electron transfer, the larger metal cations being catalysts by virtue of their greater ability to bind anions together electrostatically, or that the cation has the more fundamental role of acting as an electron mediator[21d] between the two anions in the transition state. Presently, it does not appear to be possible to distinguish between the two mechanisms. What we can do here is to note that the first mechanism is supposed to act by *decreasing* λ due to decreased electrostatic interactions between the anions by the cation binding them together and possibly lower requirements for solvent reorganization, whereas in the second one the polarizability of the cation should be the decisive factor and affect λ by increasing it with ions of decreasing polarizability (lower self-exchange rates with progressively worse mediating cations, the large tetraalkylammonium ions being particularly bad in this respect). If anything, the above rate-decrease estimates for k_1 (or $P(2)$, assuming that the nature of the cation only affects k_1) would seem to favor the latter mechanism, since a large tetraalkylammonium ion is known[27] to decrease $E°$ and is predicted to increase λ because of its inferior mediating properties vs. electrons. A value of 20 kcal mol^{-1} (corresponding to $\lambda[\mathrm{Co^{III}W/Co^{II}W}] = 31$ kcal mol^{-1}) gives a good but perhaps fortuitous agreement between theoretical and experimental rate constant ratios. The effect of adding a crown ether should have a similar effect. Of course the whole discussion above has neglected the possible influence of ion pairing upon the k_2 step. Certainly k_2 must be composed of several terms, corresponding to proton abstraction by $\mathrm{AcO^-}$, $(\mathrm{AcO^-M^+})$, $[(\mathrm{AcO})_2\mathrm{M^+}]^-$, etc., and thus possibly must be influenced by the nature of $\mathrm{M^+}$. Qualitatively, this complication does however not invalidate the analysis above.

The solvent dielectric constant should in itself influence eq 10 in two ways, namely, by affecting λ according to eq 16, where

$$\lambda = A_1 + A_2(1/D_o - 1/D) \tag{16}$$

D_o is the optical dielectric constant, equal to the square of the refractive index, and A_1 and A_2 are constants (in this context), and by affecting the electrostatic term in $\Delta G°'$. Since in the interval of dielectric constants encountered here $1/D$ can be neglected with respect to $1/D_o$, the major effect of D should be on $\Delta G°'$. With this assumption it can be shown that $\ln(k_1)$ should be quadratic in $1/D$ according to eq 17, where B_1–B_3 are constants

$$\ln(k_1) = B_1 + B_2/D - B_3/D^2 \tag{17}$$

under a set of given conditions. Moreover, insertion of the proper values of all constants and parameters in the theoretical expression for $\ln(k_1)$ shows qualitatively that B_2 and B_3 have values so as to increase $\ln(k_1)$ with decreasing D, i.e., the opposite behavior from that depicted in Figure 8. Since the k_2 step, involving the reaction between two species of opposite charge ($\mathrm{PMT}^{+\cdot}$ and $\mathrm{AcO^-}$), would also be expected to increase in rate with decreasing D, another explanation must be found for the observed $P(2)$ vs. D behavior. One explanation may be the prevalence of ion pairs of acetate ion in media of lower dielectric constant, thus nullifying the electrostatic effect on the k_2 step and decreasing the basicity of the proton-abstracting species.

The isotope effects shown in Table VI are in accordance with the mechanism proposed. It refers to abstraction of a proton from an alkylaromatic radical cation, for which isotope effects are known in a number of cases (see Table VIII and discussion below). As shown by the Marcus analysis above, it should not be possible in the system at hand to make $k_2[\mathrm{E}] \approx k_{-1}[\mathrm{Co^{III}W}]_0$ and thus make k_H/k_D approach 1; this is indeed experimentally observed for $[\mathrm{AcO^-}]$ up to 1.88 M. With water as the base, k_H/k_D is slightly higher than with $\mathrm{AcO^-}$ as the base, in agreement with the hypothesis of the transition state being more symmetric with the weaker base in this particular case (pK_a of $\mathrm{H_3O^+} = 0$, of HOAc ≈ 5, and of $\mathrm{PMT}^{+\cdot} \leq 0$).[33]

Table VIII shows k_H/k_D values for proton abstraction from alkyl aromatic radical cations, generated by either anodic oxidation or oxidation by high-potential metal ions. If we first consider anodic reactions, these are models for a mechanism involving compulsory electron transfer followed by product-determining proton abstraction from a radical cation. Provided we can assume that the k_H/k_D value reflects the structure of the transition state of the proton-transfer step, the few values available show the expected features; e.g., the more reactive radical cations show a lower k_H/k_D value vs. bases of similar strength than less reactive ones, and a more reactive base gives a lower k_H/k_D value than a less reactive one.

As noted in the introduction, unambiguous kinetic evidence for a metal ion oxidation mechanism involving reversible electron transfer/proton abstraction from an alkyl aromatic compound is only available for $\mathrm{Ce(NO_3)_6}^{2-}$ and $\mathrm{Mn(OAc)_3}$.[5,6] In the latter case it is however not yet settled whether the same difficulties as those besetting oxidations by $\mathrm{Co(OAc)_3}$[16] (formation of bi- and trinuclear complexes, ligand exchange) do not obscure the interpretation of the kinetic results. $\mathrm{Co^{III}W}$, being devoid of such complications, is an ideal reagent for the study of electron-transfer oxidation. Using k_H/k_D values for this system (Table VI) as standards, one sees that other PMT oxidations (Table VIII, oxidation by Ce(IV), Mn(III), and Ag(II)) show similar, if not within the experimental

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[33] Barek et al.[24c] gives $K \approx 10^{-5}$ for ionization of hexamethylbenzene radical cation ($\mathrm{HMB}^{+\cdot}$) in trifluoroacetic acid. If it is assumed that pK_a of $\mathrm{CF_3COOH_2}^+$ is ~ -8 (Arnett, E. *Prog. Phys. Org. Chem.* **1963**, *1*, 233) pK_a of $\mathrm{HMB}^{+\cdot}$ in water would be ca. -3. It is likely that $\mathrm{PMT}^{+\cdot}$ exhibits similar acidic properties, and hence its pK_a in water can safely be assumed to be <0.

errors identical, k_H/k_D values, further strengthening the hypothesis of a common mechanism in all these cases.

Finally a few comments on the conclusions of our exploratory study[7a] of $Co^{III}W$ oxidation of aromatics are necessary. Since it was found that *p*-nitrotoluene reduced $Co^{III}W$ at a fairly respectable rate, seemingly not in accordance with a nonbonded electron-transfer mechanism ($E°$ of *p*-nitrotoluene is estimated to be >3 V, corresponding to an extremely small k_1 values as computed by eq 10), it was proposed that electron transfer took place simultaneously with transfer of a proton from $ArCH_3$ to an oxygen of the $Co^{III}W$ shell (eq 18). This mechanism has been

$$\begin{aligned}&Co^{III}W\text{-}O\colon + H\text{-}CH_2Ar \rightleftharpoons \\ &\quad [Co^{III}W\text{-}O\colon\cdots H\text{-}CH_2Ar \leftrightarrow Co^{II}W\text{-}O\text{-}H\cdots \dot{C}H_2Ar]^{\ddagger} \rightleftharpoons \\ &\qquad\qquad Co^{II}W\text{-}O\text{-}H + \dot{C}H_2Ar \quad (18)\end{aligned}$$

suggested for the oxidation of alkyl aromatics by $Co(OAc)_3$[16] and is known as a special case of the nonbonded mechanism.[21d] Since in the case of PMT reversibility of the electron-transfer step is observed even in strongly buffered systems, it is not possible to invoke such a transition state for PMT oxidation. Rather it must be that *p*-nitrotoluene represents an extreme case where simultaneous electron/proton transfer constitutes a favorable pathway. The small experimental log (relative rate)/$\Delta G°'$ slope of -3.2 eV^{-1}, compared to a calculated one of ca. -13 eV^{-1} for the k_1 step by the Marcus treatment, is easily explicable as reflecting substituent effects upon the proton abstraction step and does not refute the mechanistic scheme of eq 1 and 2.

Conclusions

This paper describes an almost ideal model system for kinetic studies of metal ion oxidation of organic compounds, in that the metal ion reagent is not subject to the usual complexities of ligand exchange and/or formation of polynuclear species. It is thus possible to make a fairly simple analysis of the kinetic data, to study systematically the effect of variations in reactant concentrations, additives, solvent, etc., and to make an almost definitive assessment of the mechanism. The 12-tungstocobalt(III)ate ion is therefore a valuable probe for studying oxidation mechanisms of organic compounds, in particular those involving an initial reversible (or, possibly, irreversible) electron-transfer step followed by a slow chemical step. We are currently exploiting the use of 12-tungstocobalt(III)ate ion and other heteropolyions, such as those having Ni(IV), Mn(IV), and Cu(III) as the central atom, as tools in physical organic chemistry, with special emphasis on electron-transfer mechanisms.

Experimental Section

Materials. Potassium 12-tungstocobalt(III)ate was prepared according to the method given by Simmons,[13a] except that the final treatment of the salt by an ion-exchange procedure was replaced by a third recrystallization from water. Samples from three different preparations (by different persons) gave identical rate constants within the experimental error. PMT was purified by fractionation through a 40-plate column (Fischer Spaltrohr System). A middle cut of ca. 40% of the batch was used for the whole series of kinetic runs (totally ca. 600). PMT-α,α,α-d_3 was prepared according to a literature method[5a] and contained (NMR) ca. 2% of residual hydrogen in the methyl group. Water was of doubly quartz-distilled quality. All other reagents were of highest commercial quality available and were checked for reducing impurities in blind runs with $Co^{III}W$ before use.

Kinetic Runs. The appropriate solution, excluding the Co(III) species, was placed in a cuvette (3.00 mL) in the thermostated (50.0 ± 0.1 °C) cuvette compartment of a Cary 219 UV/vis spectrophotometer, equipped with Digital interface port and printer accessory. After thermal equilibration, the reaction was started by rapid addition of the $Co^{III}W$ solution (0.200 mL) and the absorbance at 390 nm recorded as a function of time. At least pentuplicate runs were made for each rate constant. The absorbance/time data were treated in accordance with the procedure described in the text. The nonlinear regression method used was that developed by Marquardt,[34] and calculations were performed on an HP-9835 table-top computer.

Stoichiometry. A solution of KOAc (0.47 M), PMT (0.094 M), and $Co^{III}W$ (2.0 mM) in 100 mL of 55/45 (w/w) $HOAc/H_2O$ was kept at 50.0 °C for 10 half-lives (ca. 4 h). Workup was performed by slowly adding the solution to a rapidly stirred slurry (under argon) of sodium bicarbonate (85 g) in water (120 mL), covered by a layer of diethyl ether (60 mL). The escaping gas was passed through a flask containing diethyl ether (100 mL) which was then used for extraction of the resulting mixture. After the mixture was washed with $NaHCO_3$ solution, the ether was distilled off through a short column and the residue subjected to GLC analysis.[7a]

Cyclic Voltammetry. Cyclic voltammetry was performed at 50 °C on a Pt electrode (sweep rate 0.1 V s^{-1}) in a three-electrode cell, using the CV equipment developed by Hammerich and Parker.[35] No IR compensation was used. The peak separation was 80 mV in both cases, and i_{pa}/i_{pc} was equal to 1 within the limits of experimental error.

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Registry No. PMT, 104-93-8; D, 7782-39-0; Sr^{2+}, 22537-39-9; Cs^+, 18459-37-5; Ca^{2+}, 14127-61-8; Rb^+, 22537-38-8; K^+, 24203-36-9; Li^+, 17341-24-1; Na^+, 17341-25-2; Me_4N^+, 51-92-3; Bu_4N^+, 10549-76-5; Pr_4N^+, 13010-31-6; Hex_4N^+, 20256-54-6; Dec_4N^+, 48078-03-1; potassium 12-tungstocobalt(III)ate, 12520-46-6.

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(34) Marquardt, D. *J. Soc. Ind. Appl. Math.* **1963**, 11. The program was purchased from Hewlett-Packard Co.

(35) Hammerich, O.; Parker, V. D. *J. Chem. Soc., Perkin Trans. 1*, **1972**, 1718.