Metal Ion Oxidation. VII.* Oxidation of Aromatic Hydrocarbons by Potassium 12-Wolframocobalt(III)ate, a "Soluble Anode"

LENNART EBERSON** and LARS-GÖRAN WISTRAND

Division of Organic Chemistry 1, Chemical Center, University of Lund, P.O. Box 740, S-220 07 Lund, Sweden

The oxidation of aromatic compounds with potassium 12-wolframocobalt(III)ate in acetic acid media has been investigated. A wide range of alkylaromatics can be acetoxylated in the α position, whereas nuclear substitution can be effected in the presence of acetate ion. In a few cases acetoxymethylation is observed, presumably *via* intermediate arylacetic acids. 4-Fluoroanisole is converted to 4-acetoxyanisole. In all preparative aspects, the reaction is closely similar to anodic and Ag(II) mediated acetoxylation.

A study of substituent effects upon α acetoxylation showed a good linear relationship between log k_{rel} and $E°$ for oxidation of the alkylaromatic substrates (slope -3.2 V^{-1}). A strong deuterium isotope effect $(k_H/k_D \approx 6)$ is indicative of a rate-determining step involving hydrogen atom transfer ("concerted electron/proton transfer") from the α C—H bond to an oxygen of the heteropoly ion.

The 12-wolframocobalt(III)ate ion ($[Co^{III}W_{12}O_{40}]^{5-}$), a member of the large family of heteropoly ions,[1] has intriguing properties which should make it useful as a mechanistic probe for studies of the oxidation of organic molecules. It consists of a cobalt(III) ion, tetrahedrally coordinated to four W_3O_{13} clusters each of which shares one oxygen with the metal ion center. The three octahedra of each cluster share edges and the four clusters share corners (the so-called Keggin structure, see Fig. 1). Thus the cobalt(III) ion is deeply buried within a shell of WO_3 octahedra and not accessible for contact with external species. It is not unreasonable to consider this type of structure as an inorganic analogue to the cryptates.

A kinetic study[2] of the electron exchange between the 12-wolframocobalt(III)ate and 12-wolframocobalt(II)ate ion showed that the WO_3 shell is stable under the conditions employed (0 °C, 0.02—0.8 M HCl in water) and that electron transfer must occur *via* an outer-sphere mechanism in the terminology of Marcus. Another reflection of the stability of the shell is the fact that no appreciable oxygen exchange took place between water and 12-wolframocobalt(III)ate ion at 25 °C in aqueous 1 M NaCl solution.[3] The standard potential of the Co(III)/Co(II) heteropoly ion couple has been
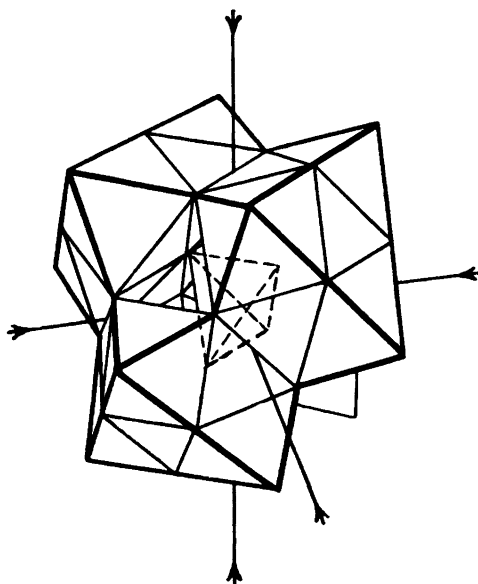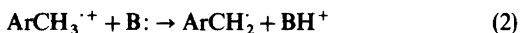

Fig. 1. The structure of the 12-wolframocobalt(III)-ate ion (the Keggin structure).

---

* Part VI, see Ref. 10.
** Author to whom inquiries should be sent.

determined to be 1.0 V *vs.* the normal hydrogen electrode[4] (NHE; all potentials mentioned in this paper are related to this reference electrode, unless otherwise noted). A similar compound, $[(H_2O)Co^{III}SiO_4W_{11}O_{36}]^{5-}$ has an $E°$ of *ca.* 1.2 V.[5]

The outer-sphere oxidant property of 12-wolframocobalt(III)ate (from now on simply denoted Co(III)W in the text) was explored by Chester[6] with respect to oxidation of alkylaromatic hydrocarbons. Under heterogeneous conditions (96 °C, neat hydrocarbon) toluene and the three xylenes were shown to give the corresponding benzaldehyde, benzyl alcohol (both formed by interference from lattice water; the salt used was $K_5[Co^{III}W_{12}O_{40}]·18H_2O$) and diphenylmethane(s), the latter being the predominant product(s). Under homogeneous conditions (acetic acid − water, 5:1) toluene gave benzyl acetate as the major product. These results were interpreted in terms of an outer-sphere electron transfer mechanism in which the initial step would be the formation of the hydrocarbon radical cation (eqn. 1), followed by proton loss from the radical cation, a second electron transfer from the benzylic radical to Co(III)W and eventual solvolysis of the carbocation (eqns. 2−4).

$$ArCH_3 + Co(III)W \rightleftharpoons ArCH_3^{·+} + Co(II)W \qquad (1)$$

$$ArCH_3^{·+} + B: \rightarrow ArCH_2^· + BH^+ \qquad (2)$$

$$ArCH_2^· + Co(III)W \rightarrow ArCH_2^+ + Co(II)W \qquad (3)$$

$$ArCH_2^+ + HOAc \rightarrow ArCH_2OAc + H^+ \qquad (4)$$

This mechanism has interesting repercussions on the general problem of electron transfer (ET) in organic chemistry. We here are presented with a case where an oxidant with $E° = 1.0$ V can oxidize a compound, toluene, with an $E°$ of 2.6 V *via* an outer-sphere ET mechanism, in spite of the fact that Marcus' theory or other ET theories predict an exceedingly slow reaction rate for a process with an $E°$ value of 1.6 V![7] In addition, we deal with a species that has been described and treated as a "conducting sphere"[1a] and hence pursuing the analogy with anodic organic electrochemistry might be a fruitful approach.

We here present evidence that Co(III)W behaves analogously to the anode as an oxidant for aromatics in almost all respects and that it can be adequately described as a "soluble anode". Its high molecular weight (*ca.* 3300) unfortunately makes

it somewhat impractical for work on any scale larger than 10 mmol, and hence we have concentrated on aspects of mechanistic interest.

RESULTS

Products. In this paper we have aimed at explorative product studies of Co(III)W oxidation of various types of aromatic compounds. A few methylaromatic compounds were selected for a more detailed study of the influence of variations in reaction conditions, especially the role of added acetate ion.

The yellow complex $K_5[Co^{III}W_{12}O_{40}]·11\,H_2O$ oxidized aromatic compounds in acetic acid − water (4/1, v./v.) at 102 °C with formation of the difficulty soluble blue complex $K_5H[Co^{II}W_{12}O_{40}]·nH_2O$ or the still less soluble $K_6[Co^{II}W_{12}O_{40}]·nH_2O$ in the presence of potassium acetate. Table 1 shows that methylaromatic compounds were oxidized in the α position to give mixtures of benzylic acetate and alcohol when acetic acid − water (medium A) was used as solvent. With 0.1 M KOAc present (medium B) the reaction was noticeably slower, and the proportion of alcohol decreased. In the case of mesitylene nuclear acetoxylation took place to a certain extent in this medium. 4-Methoxytoluene gave 21 % of the dehydrodimer, 2-(4-methoxybenzyl)-4-methylanisole, in medium A, and as expected the yield of this product decreased in the more nucleophilic medium B. In one experiment (*o*-xylene, medium D) it was noted that the addition of a small amount of trifluoroacetic acid (TFA) markedly speeded up the reaction without any significant effect on yield and product distribution.

Under non-aqueous conditions with 0.5 M KOAc present (medium C) an additional product type was the acetoxymethylated parent compound (from toluene, *p*-xylene and mesitylene). This reaction mode is known from other metal ion oxidations[8] and is generally ascribed to the sequence of reactions given in eqn. 5. We tested this hypothesis in the
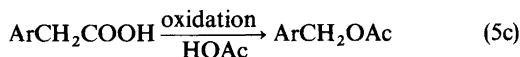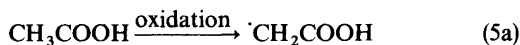
$$CH_3COOH \xrightarrow{\text{oxidation}} {}^·CH_2COOH \qquad (5a)$$

$$ArH + {}^·CH_2COOH \rightarrow ArCH_2COOH \qquad (5b)$$

$$ArCH_2COOH \xrightarrow[\text{HOAc}]{\text{oxidation}} ArCH_2OAc \qquad (5c)$$

Table 1. Oxidation of methylaromatic compounds by $K_5[Co^{III}W_{12}O_{40}].11H_2O$.

Compound	Reaction conditions[a] (time/h)	Yield/% of α-Acetate	α-Alcohol	Additional product (%)
Toluene	A (279)	14	2	
Toluene	B (216)	5	–	2-,3-,4-Methylbenzyl acetate (0.1)
Toluene	C (122)	7.5	–	2-,3-,4-Methylbenzyl acetate (6)
o-Xylene	A (49)	60	11	
o-Xylene	B (125)	32	6	
o-Xylene	C (24)	10	–	4-Methylbenzaldehyde (22)
o-Xylene	D (20)	53	6	
p-Xylene	A (8)	58	16	
p-Xylene	B (40)	47	16	
p-Xylene	C (15)	17	–	2,5-Dimethylbenzyl acetate (12)
Mesitylene	A (21)	24	5	2,4,6-Trimethylphenyl acetate (0.3)
Mesitylene	B (24)	22	6	2,4,6-Trimethylphenyl acetate (9)
Mesitylene	C (7)	20	–	2,4,6-Trimethylphenyl acetate (0.8); 2,4,6-trimethylbenzyl acetate
Hexamethylbenzene	A (0.25)	73	15	
4-Methoxytoluene	A (0.25)	59	–	2-(4-Methoxybenzyl)-4-methylanisole (21)
4-Methoxytoluene	B (0.25)	55	–	2-(4-Methoxybenzyl)-4-methylanisole (0.6)

[a] A = HOAc/H_2O 4/1 (v/v) at 102 °C; B = HOAc/H_2O 4/1 (v/v), 0.1 M KOAc at 102 °C; C = HOAc/Ac_2O 10/1 (v/v), 0.5 M KOAc at 118 °C; D = HOAc/H_2O/TFA 20/5/1 (v/v) at 100 °C.

Co(III)W case by oxidizing 4-methylphenylacetic acid and 2,4,6-trimethylphenylacetic acid by Co-(III)W in medium C which gave the corresponding acetates (eqn. 5c) in 47 and 56 % yield respectively, in a much faster process (3 – 4 h) than the Co(III)W oxidation of toluene and mesitylene. We therefore assume that the acetoxymethyl derivatives are formed *via* this route.

A few other methylaromatic compounds were run in medium A (compound, % total yield of α acetate and alcohol, reaction period/h): *m*-Xylene, 27, 24; 4-*t*-butyltoluene, 8, 6; 4-fluorotoluene, 16, 48. In addition, it is a remarkable fact that Co(III)W was completely reduced by *p*-nitrotoluene (estimated $E_{\frac{1}{2}}$ 3.1 V) in 24 h in medium C, giving as the only detectable products the corresponding aldehyde (~1 %) and α acetate (3 %). No other products have been found so far, but we plan to investigate this reaction in more detail later to see if the reason for the lack of products might be that the reaction is diverted into producing carboxymethyl radicals (*via* 4-nitrobenzyl radical attack upon HOAc).

In medium A substrates without α hydrogens (*e.g.*

anisole, naphthalene) did reduce Co(III)W but gave no identifiable low-molecular products. This behaviour is analogous to that noticed for anodic acetoxylation.[9] With acetate ion present, the analogy is extended in a way that seems to be matched by only one other metal ion oxidant, Ag(II),[10,*] but surprisingly enough not by other complexes of Co(III), like Co(III) acetate.[11] It thus became possible to obtain nuclear acetoxylation products by Co(III)W oxidation too. As an example, mesitylene, which is very prone to undergo nuclear acetoxylation anodically (nuclear to α product ratio between 4 and 20 in acetic acid/1 M potassium acetate, depending upon the nature of the electrode material),[12] was oxidized by Co(III)W or Co(III) acetate in acetic acid – water to give 3,5-dimethylbenzyl acetate exclusively. When the solution was 0.1 M in potassium acetate, Co(III)W gave a nuclear to α acetoxylation product ratio of 32:68 whereas Co(III) acetate still gave only the side-chain acetate.

* It has not been possible to run Ag(II) oxidation in the absence of acetate ion, so judgment of this aspect must await further developments.

Table 2. Nuclear substitution of aromatic compounds by $K_5[Co^{III}W_{12}O_{40}].11H_2O$ in acetic acid $-$ water (4:1, v/v) containing 0.1 M potassium acetate. Temperature 102 °C.

Compound	Yield of product/%	Isomer ratio			Isomer ratio, anodic[a]			Isomer ratio Ag(II) oxidation[b]		
		$o(\alpha)$	$m(\beta)$	p	$o(\alpha)$	$m(\beta)$	p	$o(\alpha)$	$m(\beta)$	p
Anisole	18	54	4	42	60[c]	2[c]	38[c]	68	1	31
Biphenyl	11	16	<0.1	84	31	1	68	21	<0.1	79
Naphthalene	56	99	1	—	96	4	—	95	5	—

[a] In acetic acid $-$ 1.0 M NaOAc at 25 °C, unless otherwise noted. [b] Ag(II)(bpy)$_2$S$_2$O$_8$ in acetic acid $-$ 0.5 M NaOAc at 40 °C. [c] [AcO$^-$] = 0.1 M.

A number of other substrates similarly could be acetoxylated in the nucleus by Co(III)W (see Table 2).

4-Fluoroanisole is another substrate with characteristic behaviour upon anodic oxidation in acetic acid $-$ potassium acetate, in that it undergoes displacement of fluorine by an acetoxy group.[13] This formally non-oxidative process takes place only upon anodic oxidation and can be duplicated in solution by certain silver(II) complexes.[10] Again Co(III)W displayed the same behaviour, giving a 24 % yield of 4-methoxyphenyl acetate from 4-fluoroanisole.

The rather low yields of acetoxylation products in these cases depend upon mainly two factors. The first one is the general difficulty of oxidative acetoxylations in which the products formed normally are easier to oxidize than the starting materials,[9] whereas the second one has to do with the fairly high temperature used in the Co(III)W oxidations (102 °C). Under these conditions acetate ion catalyzes the hydrolysis of aryl acetates with a concomitant decrease in yield due to the fast oxidation of phenolic derivatives. It was therefore necessary to work at low acetate ion concentration (concentrations higher than 0.2 M gave very low yields of aryl acetates) in order to obtain aryl acetates. This makes difficult the quantitative comparison with anodic oxidation, normally run at [AcO$^-$] in the range of 0.5 $-$ 1 M.

Substituent effects. In order to investigate substituent effects for α substitution competition experiments were performed for a series of substituted toluenes. The reactions were run by allowing Co(III)W compete for a ten-fold excess of each of the two substrates in acetic acid $-$ water. The results are given in Table 3, together with $E_{\frac{1}{2}}$ and, when at all possible, $E°$ values for the substrates.

Isotope effects. A number of competition experiments were also run using 4-methoxytoluene and 4-methoxy(α,α,α-$^2H_3$)toluene as substrates. By determining the deuterium content of the 4-methoxybenzyl acetate formed (MS) a k_H/k_D values of 6.0 $\pm$ 0.2 and 5.6 $\pm$ 0.2 was obtained for reaction in acetic acid $-$ water and acetic acid $-$ water $-$ 0.1 M KOAc, respectively. An experiment run under heterogeneous conditions, *i.e.*, in acetic acid where Co(III)W is insoluble, gave k_H/k_D = 5.5.

DISCUSSION

Phenomenologically, Co(III)W acetoxylation is closely similar to anodic and Ag(II) promoted acetoxylation.[9,10] The presence of acetate ion is a prerequisite for nuclear acetoxylation to occur in the two former cases and without it only α substitution takes place, if structurally possible at all. Isomer distributions are similar (see Table 1) and reactivities of different substrates closely parallel each other for all three processes. 4-Fluoroanisole

Table 3. Relative rates[a] for oxidation of substituted toluenes by $K_5[Co^{III}W_{12}O_{40}].11H_2O$ in acetic acid $-$ water (4/1, v/v) at 102 °C.
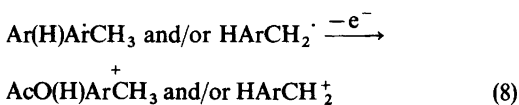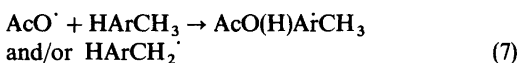
X in X$-$C$_6$H$_4$$-CH_3$	k_{rel}	log k_{rel}	$E_{\frac{1}{2}}$[b]	$E°$[c]
H	1.00	0.00	2.52	2.60
4-F	1.39	0.143	2.50	
3-CH$_3$	10.4	1.017	2.12	
4-t-Bu	69	1.839		
4-CH$_3$	94	1.973	2.10	
4-CH$_3$O	2380	3.376	1.60	1.82

[a] Corrected for statistical factors. [b] Taken from compilations in Refs. 25 $-$ 27. [c] Ref. 16.

displays identical behaviour in the three reactions. Isotope effects for α acetoxylation of 4-methoxytoluene differ however to some extent between the anodic ($k_K/k_D = 2.6$) and metal ion promoted reactions (k_H/k_D for Co(III)W and Ag(II) oxidation being 5.2 and 5.9, respectively).

In all three cases, an ET mechanism of the ECEC type[14] delineated in eqns. 1−4 has been suggested. It is pertinent to scrutinize this proposal in some detail now that the list contains one compulsory ET process (the anodic one), one that seems to leave little room for other possibilities due to the unique steric properties of the oxidant (Co(III)W) and one that by analogy has been inferred to be of the ECEC type. A few other metal ion oxidations are well worth analyzing at the same time, as well as a couple involving $SO_4^{\cdot-}$ (a very strong ET oxidant with E° for $SO_4^{\cdot-} + e^- \rightleftharpoons SO_4^{2-}$ equal to ca. 2.6 V).
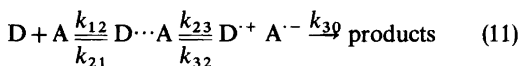
To start with the compulsory ET process, anodic acetoxylation, theoretical studies[15,16] have indicated that the direct mechanism described in eqns. 1−4 is not uniquely in accordance with all known facts. Competing indirect schemes involving acetoxy radical (eqns. 6−8 or 9−10) are feasible, albeit with the aid of the additional hypothesis that an adsorbed hydrocarbon molecule must catalyze

$$AcO^- \rightarrow AcO^{\cdot} + e^- \qquad (6)$$

$$\begin{aligned} AcO^{\cdot} + HArCH_3 &\rightarrow AcO(H)ArCH_3 \\ \text{and/or } HArCH_2^{\cdot} \end{aligned} \qquad (7)$$

$$Ar(H)ArCH_3 \text{ and/or } HArCH_2^{\cdot} \xrightarrow{-e^-}$$

$$\overset{+}{AcO(H)ArCH_3} \text{ and/or } HArCH_2^+ \qquad (8)$$

$$AcO^- \text{ and } ArH \xrightarrow{-e^-} AcO^{\cdot} + ArH^{\cdot+} \qquad (9)$$

$$AcO^{\cdot} + ArH^{\cdot+} \rightarrow AcO(H)Ar^+ \qquad (10)$$

ET from acetate ion to the anode[17] (eqn. 6). In certain situations acetoxy radical is indeed likely to intervene, e.g. by acting as an H atom abstracting species from the α position of alkylaromatics. Thus, Zavitsas-type[18] and BEBO[19] calculations of the activation energy (< 3 kcal mol^{-1}) for the model reaction $PhCH_3 + AcO^{\cdot} \rightarrow PhCH_2^{\cdot} + AcOH$ clearly show that this reaction is entirely feasible in spite of the fact that acetoxy radical has a low energy of activation for decarboxylation (6.7 kcal mol^{-1}; 1 kcal = 4.184 kJ).

It was furthermore argued[10] that Ag(II) acetoxylation of aromatics in homogeneous medium could hardly involve bimolecular coupling between a radical cation and acetoxy radical (eqns. 8−9) in view of the instability of the latter species, and this is certainly still a valid argument. The attack of acetoxy radical upon the neutral substrate (eqn. 7) is not equally implausible even for a homogeneous process[15] but can probably be excluded on grounds that thermally or photochemically generated acetoxy radical never has been observed to substitute aromatics or add onto double bonds in homogeneous solution.*

Leaving this problem aside for the moment and concentrating upon the ECEC mechanism (eqns. 1−4) as the most likely one for the anodic reaction for the moment it becomes necessary to analyze the metal ion promoted reactions in terms of current ET theory.[7] A recent communication[21] has suggested that three cases should be distinguished for the complete ET transfer scheme of eqn. 11 (D = donor = reductant; A = acceptor = oxidant), first treated by Rehm and Weller.[22] Here the first equilibrium defines the diffusion of the reactants

$$D + A \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} D \cdots A \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} D^{\cdot+} A^{\cdot-} \xrightarrow{k_{30}} \text{products} \qquad (11)$$

and the second one the ET step whereas the third step leads irreversibly to products. The steady state approach is then applied to $[D \cdots A]$ and $[D^{\cdot+} A^{\cdot-}]$ and an expression for k_p, the rate constant for the formation of products, can be derived.

Case (1) corresponds to the situation where the k_{23} step is exergonic ($\Delta G_{23}^\circ < 0$) and irreversible. These conditions, when applied to the expression for k_p lead to the well-known and well-tested prediction that k_p is essentially diffusion-controlled for ET reactions with $\Delta G_{23}^\circ < 0$; experimentally this is certainly shown to be correct for reactions with $\Delta G_{23}^\circ < -5$ kcal mol^{-1} ($\Delta E^\circ > 0.2$ V, if we chose to express free energy in units of potential). Case (2)

---

* These arguments hinge on the assumption that the acetoxy radical has identical properties when generated thermally or via ET. Recent work on the succinimidoyl radical[20] has, however, indicated that two electronically different isomers (π and σ) are possible for this type of radical, and the class of acetoxy radicals might display the same behaviour. In such case, anodically generated acetoxy radical might differ appreciably in reactivity from the thermally generated variety. This possibility does not exactly simplify mechanistic discussions in this area, but has to be considered.

has the ET step endergonic ($\Delta G_{23}^\circ > 0$) and reversible. This leads to the prediction that a plot of log k_p vs. ΔG_{23}° should be linear with a slope of $-1/2.303\ RT$ (-0.73 mol kcal^{-1} at 25 °C); if we express free energies as ΔE° values, the slope should be -16.9 V^{-1} at 25 °C. This contrasts with the original Marcus treatment[7a] where the slope of this line is predicted to be $0.5/2.303\ RT$ (-0.365 mol kcal^{-1} or 8.5 V^{-1} at 25 °C).

Case (3) has the k_{23} step endergonic and *irreversible* * ($\Delta G_{23}^\circ > 0$, $k_{23} \ll k_{21}$ and $k_{32} \ll k_{30}$). This leads to the introduction of a proportionality constant α in the relation between k_p and ΔG_{23}°, analogous to the transfer coefficient α in electrode kinetics theory, which generally takes values between 0.3 and 0.7. Thus log k_p is now predicted to be linearly correlated with ΔG_{23}°, the slope being $\alpha/2.303\ RT$. It then becomes possible to estimate values of α for case 3 reactions by dividing the experimentally measured slope by the ideal one of case 2.

Before we proceed to analyze data from metal ion oxidations, it is necessary to digress for a while to discuss which potential variable to use in correlation of k_p vs. ΔE°. Ideally one should use standard potential E°, but the problem is that we have very few reliable E° values for strongly irreversible electrode processes, like the ones corresponding to oxidation of the aromatics of Table 2 (ArH$^{\cdot+}$ + e$^-$ $\rightleftharpoons$ ArH).

It is therefore common to resort to using $E_{\frac{1}{4}}$ values, but then we must show that at least the slopes of log k_p vs. $E_{\frac{1}{4}}$ correlations are not significantly influenced by this approximation or that we can correct for it. Since the effect of irreversibility is expected to be increasingly more pronounced with increasing $E_{\frac{1}{4}}$ values (for anodic oxidation) a slope > 1 is to be expected for a plot of E° vs. $E_{\frac{1}{4}}$.

Fortunately, there exists one set of consistent experimental E° values for aromatic compounds,[24] and when these are plotted against the two sets[25,26] of consistent $E_{\frac{1}{4}}$ values that allow for inclusion of a reasonable number of data points, one finds linear correlations of the predicted form (eqns. 12 and 13). The weighted average of the slope of these two lines is 1.13, indicating that slopes of correlations

$$E^\circ = 0.32 + 1.16\ (E_{\frac{1}{4}}) \tag{12}$$
(Correlation coefficient 0.997, 12 data pairs)

$$E^\circ = 0.67 + 1.09\ (E_{\frac{1}{4}}) \tag{13}$$
(Correlation coefficient 0.981, 8 data pairs)

of log k_p vs. $E_{\frac{1}{4}}$ can be converted to slopes of log k_p vs. E_o with reasonable accuracy simply by dividing by this factor.

Another type of useful experimental potential data are ionization potentials (*IP*), shown to correlate reasonably well with $E_{\frac{1}{4}}$ values.[27] With E° the correlation obtained (eqn. 14) allows for the use of *IP* data in log k_p vs. potential plots; the desired slope

$$E^\circ = 0.73\ (IP) - 3.77 \tag{14}$$
(Correlation coefficient 0.970, 10 data pairs)

(E° as variable) is then obtained simply by dividing with the slope of the correlation given in eqn. 13.

We are now in a position to examine possible ET initiated reactions with the aid of the treatment referred to above. Table 4 lists five reactions of this type together with experimental and theoretical slopes of their log k_{rel} vs. E° relationships, the experimental slopes being obtained by use of $E_{\frac{1}{4}}$ or *IP* data and corrected to the E° scale as outlined above. Only two of the reactions (Nos. 3 and 5) would seem to qualify as ET reactions in the sense of case 2; all others have much lower values of the experimental slopes than the calculated ones and thus either must be listed as case 3 mechanisms (irreversible ET followed by a very fast chemical step) or follow other mechanisms. In view of the sometimes fairly strong kinetic deuterium isotope effects observed (see Table 3, and for further examples, Ref. 16) for metal ion oxidations, any mechanism proposed must involve transfer of a hydrogen in the rate-determining step.

In principle a kinetic deuterium isotope effect in an ET initiated reaction can have several causes. Firstly, a mechanism involving formation of a radical cation in a fast, reversible ET step, followed by a rate-determining proton transfer from the radical cation to a base should give rise to a deuterium isotope effect.[31] Both theoretical arguments and experimental facts can, however, be raised against this possibility; proton loss from radical cations — and other possible follow-up reactions, for that matter — is a fast process whereas most metal ion oxidations are over-all slow.[16] Only for very strong oxidants, *e.g.* Ag(II)

---

* It is not altogether obvious how this assumption can be reconciled with the nature of the back ET step (k_{32}); being exergonic, it should correspond to a diffusion controlled process (case 1!). The only way for k_{30} to be $\gg k_{32}$ is then that k_{30} corresponds to an extremely fast unimolecular reaction, and we may then ask ourselves if this case might not be equivalent to a concerted ET/bond cleavage step?[23]
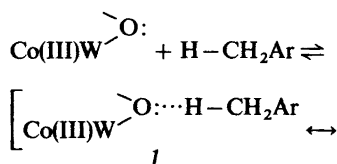
Table 4. Slope for correlations between log k_{rel} and $E°$ for suggested ET initiated oxidations of aromatic compounds.

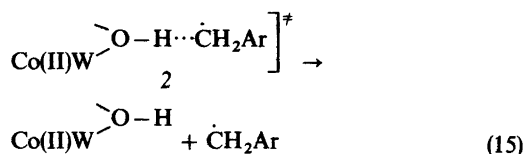| No.	Reaction	Experimental slope/V^{-1}	Correlation coefficient (number of data pairs)	Theoretical slope/ V^{-1} (temp./°C) according to Rehm-Weller	k_H/k_D	Ref.
1	$Co(III)W + ArCH_3$	-3.2^a	0.975(5)	-13.4 (102)	6.0	This work
2	$Co(OAc)_3 + ArCH_3$	-4.1^b	0.959(5)	-14.9 (65)	3.7	11
3	$Ce(IV)(NO_3)_6^{2-} + ArCH_3$	-12.6^a	0.980(6)	-17.2 (20)	1.8	28
4	$SO_4^{\cdot-} + ArCH_3$	-3.3^b	0.844(5)	-13.2 (110)	2.2	29
5	$SO_4^{\cdot-} + ArH$	$-12.9^{b,c}$	0.998(3)	-16.9 (25)		30

$^a E_{\frac{1}{2}}$ values were used as potentials. $^b IP$ values were used as potentials. ^{c} Only three data pairs were included since the remaining two lie in the diffusion controlled region.

and $SO_4^{\cdot-}$, has the ET step been shown to exhibit rates compatible with slow proton loss from the radical cation being responsible for the isotope effect. Secondly, it was recently shown[32] that benzylic deuteration, but not nuclear, can increase IP by up to about 17 mV or 0.4 kcal mol^{-1} which corresponds to $k_H/k_D \leq 2$.

Thirdly, hydrogen atom transfer, in this context more aptly described as concerted electron/proton transfer[18] and in fact better designated as a disguised case 3 reaction (see below), is an obvious possibility that would be associated with an isotope effect.[33] It is here that the unique properties of Co(III)W can be invoked to substantiate such a mechanistic proposal. It is correct that Co(III)W has a structure which completely prevents the organic reactant from coming into contact with the metal ion center and hence that H atom transfer cannot take place directly to the metal ion, but this is not a compelling argument against this mechanism.* A ligand atom, in this case an oxygen in the tungstate framework can act as an acceptor for the H atom according to eqn. 15.[34] In keeping with the ideas of inorganic ET theory the transition

$$Co(III)W \diagdown\!\!\!\overset{O:}{} + H-CH_2Ar \rightleftharpoons$$

$$\left[Co(III)W \diagdown\!\!\!\overset{O:\cdots H-CH_2Ar}{} \right] \longleftrightarrow$$
$$1$$

---

* Bond energy—bond order (BEBO) calculations clearly show that such a process is not feasible,[19] mainly due to the weakness of the Co—H bond. Calculated E_a values are above 30 kcal mol^{-1} using any reasonable set of data.

$$\left[Co(II)W \diagdown\!\!\!\overset{O-H\cdots\dot{C}H_2Ar}{} \right]^{\neq} \rightarrow$$
$$2$$

$$Co(II)W \diagdown\!\!\!\overset{O-H}{} + \dot{C}H_2Ar \qquad (15)$$

state is depicted as a hybride of two structures of identical energy,[35] differing only in the position of the electron to be transferred (Franck-Condon principle; the two transition state structures are called the reactants' and products' transition state, respectively). In the transition state, the $O:\cdots H$ (O—H) and $H-C$ (H$\cdots$C) bonds have been adjusted from their equilibrium positions so as to make structures *1* and *2* identical in energy, within the limits of the uncertainty principle *i.e.* to *ca.* 0.6 kcal mol^{-1}. Only with this condition satisfied can the electron be transferred between the two states.

This picture of the ET process rests predominantly upon ET theory of inorganic processes but is perfectly acceptable within the paradigm of organic chemistry. In the case described here an atom (H) is transferred, and in the appropriate terminology we should denote it an inner-sphere mechanism, in spite of the fact that the transferred atom is not exchanged between the inner coordination shells of two central ions. It is however necessary to modify the concept to accommodate inorganic—organic interactions in which H atom transfer normally takes place to a ligand atom and only rarely to the metal center.[36]

We thus propose that in the general case ET transfer oxidation of a C—H bond can occur according to a wide spectrum of ET/proton transfer

mechanisms, ranging from the "pure" outer-sphere variety — an electron is transferred without much reorganization of initial and final states in the transition state, giving rise to a full-fledged radical cation — to an inner-sphere mechanism in which an H atom is transferred from the C−H bond to (most likely) a ligand atom of a metal complex or other type of oxidant (*e.g.*, SO_4^{-}). Provided the ET step is the rate-determining one, the outer-sphere mechanism would occur in cases where the difference in $E°$ between oxidant and reductant is relatively small ($\Delta E°$ less than ≈ 1 V)* and be characterized by steep slopes of log k *vs.* $E°$ lines (*i.e.*, case 2 above) and weak kinetic deuterium isotope effects ($k_H/k_D \leq 2$) and the inner-sphere mechanism occur for cases with larger $\Delta E°$ values ($\Delta E° > 1$ V) and be characterized by modestly steep slopes of log $k/E°$ lines and relatively high values of k_H/k_D. The Co(III)W reaction studied in this paper fulfills all three criteria ($\Delta E°$ is as large as 0.82 V for the most easily oxidized compound, 4-methoxytoluene, the slope is −3.2, and the isotope effect 6.0 ± 0.2). We furthermore suggest that the latter type of mechanism corresponds to case 3 above and that the terminology of concerted ET/H^+ transfer is better suited (see footnote on p. 354).

It should be kept in mind that relatively little experimentation that has been consistently guided by the ideas expressed above has so far been published in the realm of inorganic−organic oxidation processes, and that it hence can be argued that we have inordinately stretched the available data. We are aware of this weakness and wish to stress the need for quantitative studies in this area specifically designed to test the applicability of current ET theory to organic systems.

EXPERIMENTAL

Materials. Potassium 12-wolframocobalt(III)ate was prepared according to the procedure given by Simmons,[4] except for the final purification process which simply consisted of three recrystallizations from hot water. Other materials and instrumental procedures have been described in a previous paper.[10]

---

* For calibration, it should be mentioned that $\Delta E° = 1$ V corresponds to an equilibrium constant for the ET step of 10^{-17} which means that the maximum possible value of the observed rate constant is of the order of 10^{-7} $M^{-1} s^{-1}$.

Oxidation of aromatics with Co(III)W. Product studies. The aromatic substrate (5.0 mmol in all cases except the two arylacetic acids where 0.5 mmol was used) and Co(III)W (1.0 mmol) was refluxed with magnetic stirring in 25 ml of stock stock solution A, B, C or D (see Table 1). After the reflux period the reaction mixture was poured into water (100 ml) and the organic material extracted with three portions of ether. The combined ether solutions were washed with saturated sodium hydrogen carbonate solution, dried with anhydrous magnesium sulfate and finally concentrated to a volume of *ca.* 2 ml by distilling off the ether through a short Vigreux column. The product distribution was analyzed by GLC/MS comparison with authentic specimen.

Competition experiments. A solution of Co(III)W (0.5 mmol) in medium A (25 ml) was heated to reflux and a mixture of the two substrates (10 mmol of each) added quickly. The workup was performed as above. The acetates were hydrolyzed (by 24 h reflux in ethanolic sodium hydroxide) and the final alcohol composition analyzed by GLC. Each pair of substrates was run twice and each run was analyzed twice.

Isotope effects. Carefully weighed amounts of a mixture of 4-methoxytoluene and 4-methoxy-(α,α,α-$^2H_3$)toluene (*ca.* 1 mmol of each) were sealed in a glass ampoule. A weighed amount of Co(III)W (0.20 mmol) was likewise sealed in a second ampoule. The substrate ampoule was then crushed in a flask containing 10.0 ml of medium A or B and the solution heated to reflux. When thermal equilibrium had been attained the Co(III)W ampoule was crushed in the solution and reflux was continued for 15 min. After the usual workup procedure the isotope composition of the 4-methoxybenzyl acetate was analyzed by GLC/MS (Finnigan 4021 mass spectrometer).

REFERENCES

1. For reviews, see a. Rasmussen, P. G. *J. Chem. Educ.* 44 (1967) 277; b. Kepert, D. L. In *Comprehensive Inorganic Chemistry*, Pergamon, Oxford 1973, Vol. 4, Chapter 51.
2. Rasmussen, P. G. and Brubaker, C. H. *Inorg. Chem. 3* (1964) 977.
3. Geier, G. and Brubaker, C. H. *Inorg. Chem. 5* (1966) 321.

4. Simmons, V. E. *Thesis*, Boston University, Boston 1963; *Diss. Abstr. 24* (1963) 1391.
5. Baker, L. C. W. and Figgis, J. S. *J. Am. Chem. Soc. 92* (1970) 3794.
6. Chester, A. W. *J. Org. Chem. 35* (1970) 1797.
7. a. Marcus, R. A. *Rev. Phys. Chem. 15* (1964) 155; b. Rehm, D. and Weller, A. *Ber. Bunsenges. Phys. Chem. 73* (1969) 834; c. Scandola, F. and Balzani, V. *J. Am. Chem. Soc. 101* (1979) 6140.
8. Heiba, E. I., Dessau, R. M. and Koehl, W. J. *J. Am. Chem. Soc. 90* (1968) 1082; *91* (1968) 138.
9. a. Eberson, L. and Nyberg, K. *J. Am. Chem. Soc. 88* (1966) 1686; b. Eberson, L. *J. Am. Chem. Soc. 89* (1967) 4669.
10. Nyberg, K. and Wistrand, L.-G. *J. Org. Chem. 43* (1978) 2613.
11. Heiba, E. I., Dessau, R. M. and Koehl, W. J. *J. Am. Chem. Soc. 91* (1969) 6830.
12. Eberson, L. and Nyberg, K. *Tetrahedron 32* (1976) 2185; *Acta Chem. Scand. B 29* (1975) 168.
13. Nyberg, K. and Wistrand, L.-G. *Chem. Commun.* (1976) 898.
14. For a recent review on mechanisms in organic electrochemistry, Eberson, L. and Nyberg, K. *Adv. Phys. Org. Chem. 12* (1976) 1.
15. Eberson, L. and Nyberg, K. *Acta Chem. Scand. B 32* (1978) 235.
16. Eberson, L., Jönsson, L. and Wistrand, L.-G. *Acta Chem. Scand. B 32* (1978) 520.
17. a. Rozhkov, I. N. *Russ. Chem. Rev. 45* (1976) 615; b. Mirkind, L. A. *Russ. Chem. Rev. 44* (1975) 999.
18. Eberson, L. and Oberrauch, E. *Acta Chem. Scand. B 33* (1979) 343.
19. Eberson, L. *Acta Chem. Scand. 34* (1980). *In press.*
20. Skell, P. S. and Day, J. C. *Acc. Chem. Res. 11* (1978) 381.
21. Schuster, G. B. *J. Am. Chem. Soc. 101* (1979) 5851.
22. Rehm, D. and Weller, A. *Isr. J. Chem. 8* (1970) 259.
23. Schmidt, S. P. and Schuster, G. B. *J. Am. Chem. Soc. In press.*
24. Parker, V. D. *J. Am. Chem. Soc. 98* (1976) 98.
25. Lund, H. *Acta Chem. Scand. 11* (1957) 1323.
26. Pysh, E. S. and Yang, N. C. *J. Am. Chem. Soc. 85* (1963) 2124.
27. Miller, L. L., Nordblom, G. D. and Mayeda, E. A. *J. Org. Chem. 37* (1972) 916 and references therein.
28. Baciocchi, E., Manolini, L. and Rol, C. *Tetrahedron Lett.* (1976) 3343.
29. Jönsson, L. and Wistrand, L.-G. *J. Chem. Soc. Perkin Trans. 1* (1979) 669.
30. Neta, P., Madhavan, V., Zemel, H. and Fessenden, R. W. *J. Am. Chem. Soc. 99* (1977) 163.
31. Andrulis, P. J., Jr., Dewar, M. J. S., Dietz, R. and Hunt, R. L. *J. Am. Chem. Soc. 88* (1966) 5473.
32. Martens, F. M., Verhoeven, J. W. and de Boer, T. J. *Tetrahedron Lett.* (1979) 2919.
33. Stewart, R. In Buncel, E. and Lee, C. C., Eds., *Isotopes in Organic Chemistry*, Elsevier, Amsterdam 1976, Vol. 2, Chapter 7.
34. Kochi, J. K. *Organometallic Mechanisms and Catalysis*, Academic, New York 1978, p. 85.
35. Reynolds, W. L. and Lumry, R. W. *Mechanisms of Electron Transfer*, The Ronald Press Co., New York 1966.
36. For a similar discussion of Co(III) perchlorate oxidations, Cooper, T. A. and Waters, W. A. *J. Chem. Soc. B* (1967) 687.