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Metal Ion Oxidation. IX.* Oxidation of Aromatic Hydrocarbons and Arylacetic Acids by Heteropoly Anions Containing Ni(IV), Mn(IV) and Co(III) Ions as Central Atoms

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Heteropoly ions containing Ni(IV) and Mn(IV) as central atoms have been shown to oxidize aromatic hydrocarbons and arylacetic acids in acetic acid and acetic acid–water, yielding acetates and alcohols. The product pattern of these reactions supports an outer-sphere electron transfer mechanism. Substituted arylacetic acids are decarboxylated when treated with 12-tungstocobalt(III)ate ion and 9-molybdonickel(IV)ate ion. These decarboxylation reactions are proposed to be outer-sphere electron transfer processes.

Recent work on the oxidation of aromatic compounds with potassium 12-tungstocobalt(III)ate, $K_5[Co(III)W_{12}O_{40}]$, [hereafter denoted Co(III)W] has demonstrated that heteropoly ions with high valent metal ions as central atoms can act as outer-sphere electron transfer reagents.[1–3] Co(III)W consists of a cobalt(III) ion buried within a shell of WO_6 octahedra and has no possibility of binding to external species.[4] Other heteropoly ions with Ni(IV) or Mn(IV) contained within a shell of nine MoO_6 octahedra may also act as outer-sphere oxidants in organic redox processes.[4] I now report that ammonium 9-molybdonickel(IV)-ate,[5] $(NH_4)_6[Ni(IV)Mo_9O_{32}]\cdot 6\ H_2O$, and ammonium 9-molybdomangan(IV)-ate,[5] $(NH_4)_6[Mn(IV)Mo_9O_{32}]\cdot 6\ H_2O$ [denoted Ni(IV)Mo and Mn(IV)Mo] can oxidize aromatic hydrocarbons and arylacetic acids in non-aqueous or aqueous media with concomitant reduction to Ni(II) and Mn(II) species [eqns. (1)–(3)].

$$ArCH_3 \xrightarrow[AcO^-]{Ni(IV)Mo\ or\ Mn(IV)Mo} ArCH_2OAc \quad (1)$$

$$ArH \xrightarrow[AcO^-]{Ni(IV)Mo} ArOAc \quad (2)$$

$$ArCH_2COOH \xrightarrow[AcO^-]{Ni(IV)Mo\ or\ Co(III)W} ArCH_2OAc + CO_2 \quad (3)$$

In a recent paper it was shown that Co(III)W also has the ability to oxidize arylacetic acids in acetic acid [eqn. (3)].[2] Hence it is possible to study the metal-ion-promoted decarboxylation of arylacetic acids by several outer-sphere oxidants. Other metal ion decarboxylations of arylacetic acids have been extensively studied, and two different mechanisms have been suggested,[6–8] one involving homolysis of a metal-carboxylate and the other electron transfer from the aromatic ring. These suggestions have mainly been based on studies of competitive decarboxylations of substituted arylacetic acids by different metal ion complexes, such as Co(III), Ce(IV) and Cu(III), which can form a ligand-to-metal bond to the acid (inner-sphere mechanism).

In order to compare outer-sphere decarboxylation with these inner-sphere decarboxylations, a

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* Part VIII, see Jönsson, L. *Acta Chem. Scand. B 35* (1981) 683.

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series of competitive oxidations by Co(III)W and Ni(IV)Mo has been studied. The results indicate that decarboxylations by Ni(IV)Mo, Co(III)W, Co(III)(OAc)$_3$, Cu(III) and Ce(IV) follow an outer-sphere electron transfer mechanism.

RESULTS

Oxidation of aromatic hydrocarbons. The Ni(IV)Mo and Mn(IV)Mo complexes were soluble in water and acetic acid–water, but insoluble in glacial acetic acid. The Ni(IV)Mo complex was slowly reduced and hydrolyzed in water or acetic acid–water at room temperature, whereas the Mn(IV)Mo complex was stable against hydrolysis and redox processes induced by these media below 60 °C. In connection with these qualitative studies of the redox stability of the heteropoly anions, the potential of the Mn(IV)/Mn(III) or Mn(II) heteropoly ion couple has been determined to be 1.4 V *vs.* NHE by cyclic voltammetry. It was impossible to obtain a value for the Ni(IV)/Ni(II) couple by this method. Latimer gives[9] an E_0 value of 1.8 V for Ni(IV)O_4^{2-}/Ni(II), and it is reasonable that Ni(IV)Mo also has this high oxidizing power.

In spite of the instability of Ni(IV)Mo in acetic acid–water it was possible to oxidize 4-methoxytoluene in this medium, resulting in a moderate yield (44 %) of the corresponding benzyl acetate and alcohol. With 0.5 M KOAc present in glacial acetic acid, the yields of acetate and aldehyde increased to 51 % and 13 %, respectively, and the proportion of alcohol decreased. The results of these and other oxidations of 4-methoxytoluene by Ni(IV)Mo and Mn(IV)Mo are presented in Table 1. Toluene gave 40 % benzyl acetate and 10 % benzaldehyde on oxidation by Ni(IV)Mo (in acetic acid-0.5 M KOAc), whereas 4-nitrotoluene completely reduced Ni(IV)Mo, but gave no detectable products. This remarkable behaviour was also noted for Co(III)W

Table 1. Acetoxylation of 4-methoxytoluene by Ni(IV)Mo and Mn(IV)Mo under different conditions.[a]

Reagent	Reaction conditions	Yield/ %[b]		
		4-Methoxybenzyl acetate	4-Methoxybenzaldehyde	4-Methoxybenzyl alcohol
Ni(IV)Mo	HOAc/H_2O (4:1 v/v)	44	2	9
Ni(IV)Mo	HOAc/H_2O (1:1 v/v)	21	4	28
Mn(IV)Mo	HOAc/H_2O (1:1 v/v)	20	6	25
Ni(IV)Mo	HOAc	42	13	7
Ni(IV)Mo	HOAc, 0.5 M KOAc	51	13	<1
Mn(IV)Mo	HOAc, 0.5 M KOAc	7	1	<1

[a] Reaction conditions: 4-Methoxytoluene (4 mmol), reagent (0.2 mmol), solvent (10 ml), reflux temperature, reaction period 2 h under an argon atmosphere. [b] GLC based on Ni(IV) or Mn(IV).

Table 2. Nuclear acetoxylation of aromatic compounds by Ni(IV)Mo.[a]

Compound	Yield of nuclear acetates/%[b]	Isomer distribution This work			Co(III)W oxidation[c]			Anodic oxidation[d]		
		o	*m*	*p*	*o*	*m*	*p*	*o*	*m*	*p*
Anisole	13	53	5	42	54	4	42	60	2	38
Biphenyl	40	18	<0.1	82	16	<0.1	84	31	1	68

[a] Reaction conditions, unless otherwise noted: Aromatic compound (1 mmol), Ni(IV)Mo (0.2 mmol), glacial acetic acid containing 0.5 M KOAc (5 ml) acetic anhydride (1 ml) reflux temperature, reaction period 1 h. [b] GLC yield based on Ni(IV). [c] In acetic acid–water (4:1 v/v) containing 0.1 M KOAc, temperature 102 °C, Ref. 2. [d] In acetic acid–water – 1.0 M NaOAc (in anisole oxidation [OAc^-]=0.1 M) at 25 °C, Ref. 2.

Table 3. Relative rates of Co(III)W and Ni(IV)Mo oxidation of substituted arylacetic acids in acetic acid-KOAc.[a]

Substituent	Relative rate[b] Co(III)W	Ni(IV)Mo
p-OCH_3	2200±500	44.6±1
m-OCH_3	69.4±4	7.1±0.2
p-Ph	14.8±3	2.6±0.1
p-CH_3	2.00±0.08	1.95±0.02
m-CH_3	1.28±0.05	1.15±0.02
H	1.00	1.00
p-Cl	0.36±0.05	1.00±0.02
m-Cl	0.25±0.04	0.55±0.05

[a] Reaction conditions: Substituted arylacetic acid (2 mmol), phenylacetic acid (2 mmol), potassium 12-tungstocobalt(III)ate or ammonium 9-molybdonickel(IV)ate (0.1 mmol), glacial acetic acid−0.5 M KOAc (10 ml) (at Ni(IV) oxidation glacial acetic acid −1 M KOAc (10 ml) and acetic anhydride (2 ml)), reflux temperature, reaction period 2 h under an argon atmosphere. [b] Values given are the average of two or four independent experiments, each analyzed twice by GLC.

oxidation.[2]

Under non-aqueous conditions with 0.5 M KOAc present, substrates without α hydrogen gave nuclear acetoxylation (see Table 2). The isomer distribution is analogous to that observed for Co(III)W and anodic acetoxylation.[2] In all reactions above, and in the decarboxylation reactions, Ni(IV)Mo was reduced to a weak blue-green coloured 6-heteropoly anion, containing Ni(II). The Mn(IV)Mo was reduced to Mn^{2+} during decomposition of the heteropoly anion.

Isotope effects. The kinetic isotope effect was determined for the Ni(IV)Mo α acetoxylation of toluene and 4-methoxytoluene by allowing Ni(IV)Mo to react with a large excess of an equimolar amount of protiated and deuterated compound. By determining the deuterium contents (MS) of the benzyl acetates, a k_H/k_D value of 4.2±0.1 and 2.7±0.1 was obtained for toluene and 4-methoxytoluene, respectively.

Decarboxylation of arylacetic acids. The oxidative decarboxylation of arylacetic acids by Co(III)W and Ni(IV)Mo in refluxing acetic acid, containing 0.5 M KOAc and acetic anhydride, resulted in the formation of benzyl acetates, which accounted for more than 80 % of all products observed. An attempt to decarboxylate 4-nitrophenylacetic acid by Co(III)W and Ni(IV) gave no detectable products, but the reagents were completely reduced within 2 h.

Competitive experiments. Competitive decarboxylations of a series of substituted arylacetic acids by Co(III)W and Ni(IV)Mo were carried out. The relative rates were determined from the relative amounts of the corresponding benzyl acetates produced. (For results and reaction conditions, see Table 3.) Excluding the rate constants for the methoxy and phenyl compounds, which appear to be abnormally high, the logarithms of the relative rates were plotted against the substituent constants[10] σ and σ^+ and gave a ρ value of −1.71 (r=0.997) and a ρ^+ value of −0.77 (r=0.985) for Co(III)W and Ni(IV)Mo decarboxylation, respectively. If the data for the methoxy and phenyl compounds are included, the correlation is not significant. Correlation of the logarithms of the relative rates for Ni(IV)Mo decarboxylation against σ gave no significant correlation. The logarithms of the relative rates of Ni(IV)Mo decarboxylation were also plotted against the logarithms of the relative rates of Co(III)W, Co(III)$(OAc)_3$, Cu(III) and Ce(IV) decarboxylation. Data from this work, and Refs. 7, 8 and 6b, respectively. See Figs. 1−4.

DISCUSSION

The results of the Ni(IV)Mo and Mn(IV)Mo oxidation of aromatic hydrocarbons show that the product and isomer distributions are in conformity with those obtained in the acetoxylation of the same compounds by established electron transfer reagents such as anodic,[11]

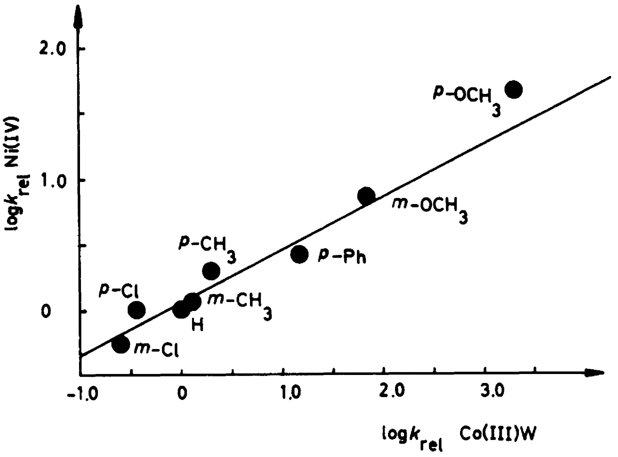

Fig. 1. Plot of log k_{rel} of decarboxylation by Ni(IV)Mo *vs.* log k_{rel} of decarboxylation by Co(III)W. Slope=0.40 (r=0.97).

Ce(IV),[12] Ag(II)[13] and 12-tungstocobalt(III)ate ion[2] (Co(III)W). (See Tables 1 and 2.) The relatively large amount of aldehydes produced in acetic acid–acetate ion media is due to geminal bis-acetoxylation of methyl arenes yielding $ArCH(OAc)_2$, followed by decomposition in GLC to aldehydes. This reacion is well-known from other electron transfer acetoxylations of alkyl-aromatic compounds.[11]

The observed primary kinetic isotope effects (toluene, k_H/k_D=4.2, 4-methoxytoluene, k_H/k_D=2.7) are in accord with a mechanism including an electron transfer step, followed by a rate-limiting proton transfer step. (For a discussion of the isotope effect in an electron transfer initiated reaction followed by proton transfer, see Refs. 2a and 14.)

Since Ni(IV)Mo and Mn(IV)Mo are inert to substitution they are able to oxidize aromatic compounds *via* an electron transfer initiated reaction with no bridging ligand between the oxidant and reductant in the transition state.

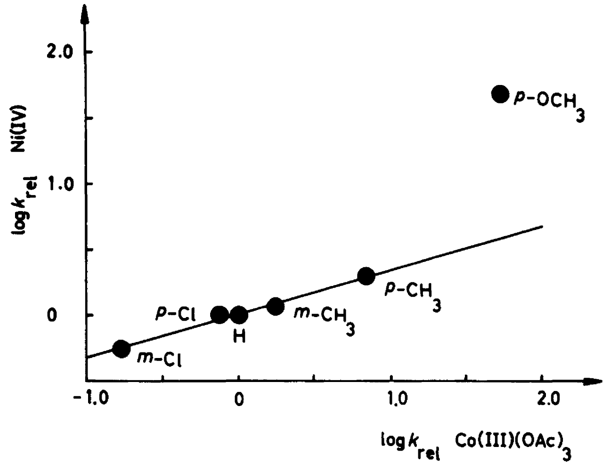

Fig. 2. Plot of log k_{rel} of decarboxylation by Ni(IV)Mo *vs.* log k_{rel} of decarboxylation by $Co(III)(OAc)_3$. Slope=0.33 (r=0.99).

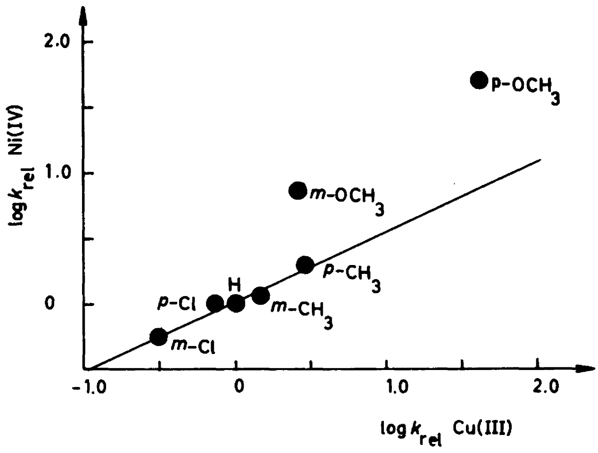

Fig. 3. Plot of log k_{rel} of decarboxylation by Ni(IV)Mo *vs.* log k_{rel} of decarboxylation by Cu(III). Slope=0.54 (r=0.98).

In the light of these results and the properties of the reagents, a mechanism, analogous to that for Co(III)W acetoxylation, involving a reversible electron transfer step followed by a rate-limiting proton transfer step, is most probable (eqns. (4)−(7)).

$$ArCH_3 + M(IV)Mo \rightleftharpoons ArCH_3^{\cdot +} + M(III)Mo \quad (4)$$

$$ArCH_3^{\cdot +} + B \rightarrow ArCH_2^{\cdot} + HB^+ \quad (5)$$

$$ArCH_2^{\cdot} + M(III)Mo \rightarrow ArCH_2^+ + M(II)Mo \quad (6)$$

$$ArCH_2^+ + Nu^- \rightarrow ArCH_2Nu \quad (7)$$

However, this mechanism is more complicated than Co(III)W acetoxylation, since Co(III)W is a one-electron reagent. Ni(IV)Mo and Mn(IV)Mo are two-electron reagents, and an intermediate M(III)Mo species can act as oxidant ion in both steps 1 and 3, in competition with M(IV)Mo.

We therefore need more quantitative information about these reactions, such as kinetic data, the effect of additives *etc.*, to establish a definitive mechanism. We have now also begun to

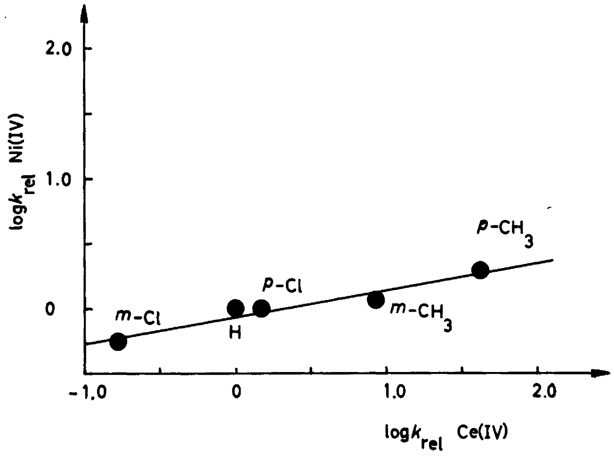

Fig. 4. Plot of log k_{rel} of decarboxylation by Ni(IV)Mo *vs.* log k_{rel} of decarboxylation by Ce(IV). Slope=0.21 (r=0.97).

investigate the remarkable fact that Co(III)W and Ni(IV)Mo are completely reduced by media containing 4-nitrotoluene or 4-nitrophenylacetic acid, with no detectable products so far.

The relative rates calculated in Co(III)W and Ni(IV)Mo initiated decarboxylation of arylacetic acids containing electron-releasing substituents are very high, based on expectations derived from the Hammett correlations (see Table 3). These results are in agreement with work on Ce(IV) and Cu(III) promoted decarboxylation of arylacetic acids.[6b,8]

To explain these observations Trahanovsky *et al.* suggested two mechanistic pathways for Ce(IV) decarboxylation of arylacetic acids.[6b] Acids which give a good Hammett correlation (see Table 4) are suggested to follow a pathway involving homolysis of a metal-carboxylate complex (inner-sphere complex). The unusually rapid rates of oxidation of both 3- and 4-methoxyphenylacetic acids suggest that these acids are oxidized *via* a mechanism involving initial formation of the radical cation of the aromatic ring. The analogous results obtained in Cu(III) initiated decarboxylation were explained in the same manner.[8]

Since it is impossible to form an inner-sphere complex between Co(III)W or Ni(IV)Mo and the substrate, one of these explanations is not relevant for the decarboxylations described in this paper. The results instead show that two different outer-sphere electron transfer mechanisms must exist. One mechanism is assumed to involve an electron transfer from the aromatic ring in arylacetic acids containing electron-rich substituents (Scheme 1).

Table 4. ρ-Values for decarboxylation of arylacetic acids by different oxidants.

Oxidant	ρ	ρ^+	Ref.
$SO_4^{\cdot -}$	-0.60^a	-0.44^a	17
Ce(IV)		-2.9	6b
Co(III)		-2.9^a	7
Cu(III)		-1.4	8
Co(III)W	-1.7		This work
Ni(IV)Mo		-0.77	This work

[a] The correlation includes results from arylacetic acids containing electron-releasing substituents.

$$\mathrm{ArCH_2COOH} \xrightarrow{M^{n+}} \mathrm{Ar}^{\cdot}\overset{+}{\mathrm{C}}\mathrm{H_2COOH}$$

$$\xrightarrow{\text{fast}} \mathrm{ArCH_2}^{\cdot} + \mathrm{CO_2} + \mathrm{H^+}$$

$$\mathrm{ArCH_2}^{\cdot} \xrightarrow{M^{n+}} \mathrm{ArCH_2}^{+} \xrightarrow{Nu^-} \mathrm{ArCH_2Nu}$$

Scheme 1.

Another pathway involves a Kolbe-like (anodic oxidation of carboxylic acids) mechanism *via* an electron transfer from the carboxylic group, possibly with concerted loss of carbon dioxide (Scheme 2).

$$\mathrm{ArCH_2COOH} \xrightarrow[-H^+]{M^{n+}} \mathrm{ArCH_2COO}^{\cdot} \longrightarrow$$

$$\mathrm{ArCH_2}^{\cdot} + \mathrm{CO_2}$$

$$\mathrm{ArCH_2}^{\cdot} \xrightarrow{M^{n+}} \mathrm{ArCH_2}^{+} \xrightarrow{Nu^-} \mathrm{ArCH_2Nu}$$

Scheme 2.

Compounds following this pathway contain less electron-releasing substituents and follow a good Hammett correlation. The ρ-values in these correlations are -1.71 and -0.77 for Co(III)W and Ni(IV)Mo decarboxylation, respectively, indicating a process leading to a benzyl radical in the rate-determining step. It is known that ρ-values for most such processes are in the range of -0.3 to -1.5.[6b,15,16]

A comparison between the values in Table 4 shows that the ρ-values for decarboxylation of more electron-poor acids by Co(III)W, Ni(IV)-Mo, Cu(III)[8] and $SO_4^{\cdot -}$ [17] support an electron transfer mechanism without a metal-carboxylate intermediate. The plots of the logarithms of the relative rates for Ni(IV)Mo, Co(III)W, Co(III)(OAc)$_3$, Cu(III) and Ce(IV) decarboxylations against each other (see Figs. 1–4) give good linear correlations except for the *para-* and *meta*-methoxy compounds. This is good support for a Kolbe-like mechanism, involving outer-sphere electron transfer for all these decarboxylation reactions.[18] The deviation of methoxy compounds from the linear plots indicate, even if the deviation in some cases is not clearly significant, that these acids follow a mechanism with electron transfer from the aromatic ring. In the light of this, it is probable that Ce(IV) decarboxylation

Table 5. Rate constants for decarboxylation of 4-methoxyphenylacetic acid together with different parameters in eqn. 8.[a]

Oxidant	k_{obs}/M^{-1} s^{-1}	k_{calc}/M^{-1} s^{-1}	λ/kcal mol^{-1}	W/kcal mol^{-1}	$\Delta G^{o'}$/kcal mol^{-1}
Co(III)W	~0.5	0.08	31.5	3.3	16.3
Ni(IV)Mo	fast	$8 \cdot 10^4$	32.5	4.0	−2.8

[a] All parameters are based on data and methods given in Ref. 14. $\Delta G^{o'}$ values are based on E^o for Co(III)/Co(II)=1.0 V (Ref. 14), E^o for Ni(IV)/Ni(II)=1.8 V (Ref. 9) and E_p for 4-methoxyphenylacetic acid=1.85 V (Ref. 19), all values *vs.* NHE.

proceeds *via* electron transfer instead of a process involving a metal-carboxylate intermediate, which was suggested by Trahanovsky *et al.*[6b]

A comparison between crude estimated rate constants (k_{obs}) based on observations in connection with competition experiments for Co(III)W and Ni(IV)Mo decarboxylation shows good agreement with calculated rate constants (k_{calc}) from eqn. (8), which is based on the Marcus theory for the outer-sphere electron transfer processes.* [See Table 5 and eqn. (8)].In eqn. (8), k_d is assumed to be $2 \cdot 10^{10}$ M^{-1} s^{-1}, A=constant with a value of 0.2, W is the electrostatic work expended to bring the two reactants together, corrected for ionic strength (μ=0.5). λ is the reorganization energy of the reaction and $\Delta G^{o'}$ is the free energy change of the reaction corrected by a term involving the electrostatic energy (W).

$$k_{calc} = \frac{k_d}{1 + A \exp\left\{\left[W + \frac{\lambda}{4}\left(1 + \frac{\Delta G^{o'}}{\lambda}\right)^2\right]/RT\right\}} \qquad (8)$$

The relatively good agreement between observed and calculated rate constants lends additional support for an outer-sphere electron transfer mechanism for Co(III)W and Ni(IV)Mo decarboxylation of arylacetic acids.

EXPERIMENTAL

Materials. Ammonium 9-molybdonickel(IV)-ate and ammonium 9-molybdomangan(IV)ate were prepared according to a literature method,[5] and were recrystallized twice from hot water (70 °C). Potassium 12-tungstocobalt(III)ate was prepared according to the procedure given by Simmons,[20] and was recrystallized three times from hot water. All other chemicals used in this investigation were either purchased of the highest quality available or prepared according to known methods described in earlier work.[11,21,22] 4-Biphenylacetic acid, 4-nitrophenylacetic acid, and 3-chlorophenylacetic acid were recrystallized twice from ethanol−water.

Oxidation procedure. A mixture of the aromatic compound, heteropoly ion and the solvent was stirred at reflux temperature under an argon atmosphere. The mixture was worked up by addition to saturated sodium hydrogen carbonate solution, followed by ether extraction and GLC analysis. The competition experiments were carried out in the following way: 2 mmol of each of two arylacetic acids were heated at reflux temperature in a solvent−reagent mixture for 2 h under an argon atmosphere. The work-up procedure was the same as above.

Analysis. Yields and isomer distributions were determined using a Varian 1400 gas chromatograph equipped with an electronic integrator (Hewlett-Packard 3380 A), on a 2 m×3 mm 5 % NPGS on Chromosorb W and a 2 m×3 mm 3 % OV 101 on Chromosorb Q column. The yield was determined using an internal standard (hexamethyl-benzene and bimesitylene) calibrated against authentic samples. The identification of the products was based on GLC-MS comparison (Finnigan 4021 instrument) with authentic samples. The isotope effect was determined by mass spectroscopy.

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