Metal Ion Oxidation. VIII.* Oxidation of Organic Compounds by Copper(III)

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The copper(III) complex of biuret [potassium bis-(biuretato)cuprate(III), *1*] has been shown to oxidize aromatic and alicyclic compounds in acetic and trifluoroacetic acid, yielding acetates and dehydro dimers. The product pattern of these reactions supports an electron transfer mechanism. Aryl halides, *e.g.* fluorobenzene, are hydrolyzed to phenols and the mechanism is postulated to be an electron transfer chain mechanism, the $S_{ON}2$ mechanism. Substituted arylacetic acids are decarboxylated when treated with *1* in acetic acid at reflux temperature. This decarboxylation is proposed to be a one-electron process, the rate-determining step being the decomposition of an arylacetic acid-copper(III) complex to a benzylic radical.
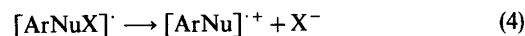
It has been suggested, although without experimental evidence, that copper(III) species mediate the oxidation of organic compounds by a strong oxidant, such as peroxydisulfate[1−3] in the presence of copper(II).** Several copper(III) complexes are known, *e.g.*, peptide,[4] periodate[5,6] and bis-biuret complexes[7] and the redox properties of peptide complexes have been extensively studied by Margerum *et al.* Hence possibilities exist to study the direct oxidation of organic compounds by copper-(III) ion.

The copper(III) state is greatly stabilized by the ligands in its complexes, but the copper(III) ion can

be activated by aqueous as well as non-aqueous acids and act as a strong oxidant.[4,8] The $E°$ value for copper(III)$_{aq}$/copper(II)$_{aq}$ is given as ≥ 1.8 V, and is probably higher in non-aqueous media, such as trifluoroacetic acid (TFA).[9] These properties make it possible to use copper(III) as a potent oxidant in non-aqueous acid solvents. All previous organic oxidations by copper(III) complexes have been confined to aqueous media, but recently we have reported that *1* can oxidize organic compounds in non-aqueous media or in media with low concentrations of water present.[8] A remarkable reaction under these conditions is the copper(III) promoted hydrolysis of fluoro- and chlorobenzene in TFA (eqn. (1), ArX = PhF or PhCl). It was suggested that this

$$ArX \xrightarrow[\text{TFA/H}_2\text{O}]{\text{Cu(III)}} ArOH \qquad (1)$$
$$\text{yield } 35-50 \text{ \%}$$
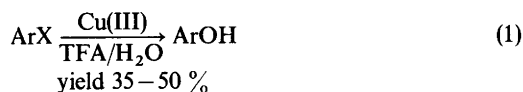
reaction might be initiated by an electron transfer step between copper(III) and the aryl halide, followed by an electron transfer chain mechanism, the $S_{ON}2$ mechanism [eqns. (2)−(5)].[8,10] A discus-
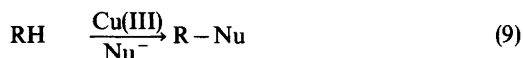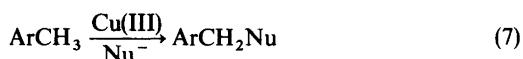
$$ArX \longrightarrow [ArX]^{·+} + e^- \qquad (2)$$

$$[ArX]^{·+} + Nu^- \longrightarrow [ArNuX]^{·} \qquad (3)$$

$$[ArNuX]^{·} \longrightarrow [ArNu]^{·+} + X^- \qquad (4)$$

$$[ArNu]^{·+} + ArX \longrightarrow ArNu + [ArX]^{·+} \qquad (5)$$

sion of and experimental evidence for the $S_{ON}2$ mechanism are given in Refs. 10−12.

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* Part VII, see Eberson, L. and Wistrand, L.-G. *Acta Chem. Scand. B 34* (1980) 349.
** As an example, it is claimed in Ref. 3 that copper(III) acts as an intermediate in the oxidation of *p*-methoxytoluene to *p*-methoxybenzaldehyde by peroxydisulfate in the presence of copper(II). This proposal may be correct, since complex *1* promotes the same reaction under similar conditions.

Complex *1* has also the ability to oxidize aryl-acetic acids, aromatic and alicyclic compounds to the usual range of oxidative substitution and coupling products expected for metal ion oxidation [eqns. (6)−(10)].[13]

$$\text{ArH} \quad \xrightarrow[\text{Nu}^-]{\text{Cu(III)}} \text{ArNu} \tag{6}$$

$$\text{ArCH}_3 \quad \xrightarrow[\text{Nu}^-]{\text{Cu(III)}} \text{ArCH}_2\text{Nu} \tag{7}$$

$$\text{ArCH}_3 \quad \xrightarrow{\text{Cu(III)}} \text{CH}_3\text{ArArCH}_3 + \text{ArCH}_2 - \text{Ar}' \tag{8}$$

$$\text{RH} \quad \xrightarrow[\text{Nu}^-]{\text{Cu(III)}} \text{R} - \text{Nu} \tag{9}$$

$$\text{ArCH}_2\text{COOH} \xrightarrow[\text{HOAc}]{\text{Cu(III)}} \text{ArCH}_2\text{OAc} + \text{CO}_2 \tag{10}$$

As a prelude to detailed mechanistic studies this paper reports the phenomenology of these reactions.

RESULTS

Preparative experiments. Different types of organic compounds were reacted with copper(III) complexes of biuret in TFA or acetic acid/TFA mixtures (results and reaction conditions, see Table 1). Methylbenzenes were oxidized to benzylic acetates in moderate yields. These substrates also gave very small amounts of nuclear acetates. Strongly activated methylbenzenes, *e.g.*, *p*-methoxytoluene, reacted very fast but gave only a small amount of side-

Table 1. Oxidation of some organic compounds by Cu(III) complex of biuret in acetic acid − TFA.[a]

Compound (exp. No)	Main products, yield/%[c]	Other products,[b] yield/%[c]
Toluene (1)	Benzyl acetate, 2	Cresyl acetate, 0.3; benzaldehyde, 0.3
p-Xylene (2)	*p*-Methylbenzyl acetate, 33	2,5,4′-Trimethyldiphenylmethane, 1
p-*tert*-Butyltoluene (3)	*p*-*tert*-Butylbenzyl acetate, 28	*p*-*tert*-Butylbenzaldehyde, 0.1
p-Methoxytoluene (4)	*p*-Methoxybenzyl acetate, trace	
Mesitylene (5)	3,5-Dimethylbenzyl acetate, 28	Mesityl acetate, 0.2; 3,5-dimethylbenzaldehyde, 0.1
Mesitylene (6)	2,4,6,3′,5′-Pentamethyldiphenylmethane, 5	Bimesitylene, 0.1
Mesitylene (7)	2,4,6,3′,5′-Pentamethyldiphenylmethane, 24	Bimesitylene, 7
Mesitylene + naphthalene (1:1) (8)	1-Mesitylnaphthalene, 28	Dimesitylnaphthalene, 7; dimers of mesitylnaphthalene, 8; pentamethyldiphenylmethane and binaphthyl, traces
Naphthalene (9)	1-Naphthyl acetate, 10	
Benzene (10)	Phenol, 11	
Anisole (11)	Acetoxymethyl phenyl ether, 15	Phenol, trace
p-Anisylmercury(II) acetate (12)	*p*-Methoxyphenyl acetate, 18 *o*-Methoxyphenyl acetate, 2	Anisole, trace Phenol, trace
Cyclohexane (13)[d]	3-Cyclohexenyl acetate, 7	Cyclohexanol and cyclohexanone, trace
Cyclohexane (14)[d]	3-Cyclohexenyl acetate, 3	Cyclohexanol and cyclohexanone, trace
Adamantane (15)	1-Adamantyl acetate, 26 2-Adamantyl acetate, 4	
Phenylacetic acid (16)	Benzyl acetate, 33	Benzaldehyde, trace

[a] Conditions used in all experiments, unless otherwise noted: substrate (5 mmol), potassium bis(biuretato)cuprate(III) (10 mmol), glacial acetic acid (25 ml), TFA (2.5 ml), reflux temperature, reaction period 2 h. Reaction medium in experiments 6 and 8 was TFA (25 ml), in experiment 7 TFA (25 ml) and mesitylene (12.5 ml). The substrates in experiment 8 were mesitylene (5 mmol) and naphthalene (5 mmol). Reaction medium in experiment 10 was TFA (25 ml) and water (5 mmol). [b] Small amounts of organic trifluoroacetates were formed in all experiments. [c] GLC yield based on Cu(III). [d] Substrate (30 mmol).

chain acetate. The methylbenzenes were oxidized to dehydrodimers (biaryls and diphenylmethanes) in TFA (expts. 6 and 7) and addition of excess substrate increased the yield (expt. 7). It was also possible to obtain mixed biphenyls by oxidative cross-coupling of two aromatic compounds (expt. 8). Oxidation of substrates without any α hydrogen available for substitution gave a more complex product pattern. Naphthalene gave 1-naphthyl acetate in rather low yield (expt. 9). Anisole gave substitution at the methoxy group only (expt. 11). Benzene was hydroxylated in a medium of TFA-water, but did not give any detectable products in acetic acid. A strongly activated compound, diphenyl ether, reacted with *1* in TFA to give phenoxybenzamide.

Since copper(III) is isoelectronic with palladium-(II), which is known to promote formation of aryl acetates from arylmercury compounds *via* a trans-metallation pathway, it was of interest to investigate if copper(III) reacts with arylmercury compounds in the same manner.[13] Experiment 12 shows that *p*-anisylmercury(II)acetate gave aryl acetate isomers with almost the same isomer distribution as that of the starting material. Cyclohexene and cyclohexane gave a low yield of 3-cyclohexenyl acetate (expts. 13 and 14). As expected, adamantane gave adamantyl acetates (expt. 15). The oxidative decarboxylation of benzoic acid by copper(III) failed, but decarboxylation of arylacetic acids in acetic acid resulted in the rapid formation of benzyl acetates (see expt. 16 and Table 3). To test if it was possible

to replace copper(III) with other trivalent metal complexes, a nickel(III) biuret complex was tried in the oxidation of methylbenzenes and under comparable reaction conditions this complex transformed methylbenzenes to diphenylmethanes and biaryls.

Copper(III) also promotes halogen/hydroxyl exchange of aryl halides in TFA-water at reflux temperatures (results and reaction conditions, see Table 2). The main products in these reactions were phenols derived from halogen/hydroxyl exchange but the reaction also gave ordinary oxidative hydrogen/hydroxyl substitution in low yield. Also small amounts of polychlorinated compounds and quinones are observed. Note that the addition of an excess of the aryl halide results in a halogen/aryl exchange (expt. 19). The high yields of the *p*-halogenophenols in expts. 21 and 23 show that these reactions are definitely catalytic in copper(III). The product distribution in expts. 21 and 24 shows that loss of fluorine is much favoured over loss of chlorine and bromine.

Finally, control experiments in this and previous work[14] showed that the reactions described here do not take place in the absence of copper(III) or in the presence of copper(II) only.

Isotope effects. The kinetic isotope effect was determined for the α acetoxylation of *p*-xylene and hydroxylation of benzene by allowing *1* to react with a large excess of an equimolar amount of protiated and deuterated compound. By determining the deuterium contents of the products a

Table 2. Oxidation of some aryl halides by Cu(III) complex of biuret in trifluoroacetic acid.[a]

Aryl halide (exp. No.)	Yield/%[b] Phenols			Other products
	o	*m*	*p*	
Chlorobenzene (17)	6	<0.1	7	Phenol, 35
Fluorobenzene (18)	1	<0.1	1	Phenol, 44
Fluorobenzene (19)[c]	—	—	—	Fluoribiphenyl (*o/p* = 70/30), 2
o-Chlorofluorobenzene (20)	trace			
p-Chlorofluorobenzene (21)	—	—	90[d]	*p*-Benzoquinone, 4
m-Dichlorobenzene (22)	—	10	—	2,4-Dichlorophenol, 13
p-Dichlorobenzene (23)	—	—	132	*p*-Benzoquinone, 1,2,4-trichlorobenzene, and 2,5-dichlorophenol, trace
p-Bromofluorobenzene (24)	—	—	10[e]	Tribromobenzene, trace

[a] Conditions used in all experiments, unless otherwise noted: Aryl halide (10 mmol), potassium bis(biuretato)cuprate(III) (5 mmol), water (5 mmol), TFA (25 ml), reflux temperature, reaction period 2 h. [b] GLC yield based on Cu(III). [c] Reaction medium in this experiment: TFA (12.5 ml) and fluorobenzene (12.5 ml). [d] Product distribution: *p*-Fluorophenol 37% and *p*-chlorophenol 63%. [e] Product distribution: *p*-fluorophenol 36% and *p*-bromophenol 64%.

Table 3. Relative rate of Cu(III) oxidation of substituted arylacetic acids in acetic acid.[a]

Substituent	Relative rate[b]
p-OCH$_3$	39.2 ± 0.5
p-CH$_3$	2.90 ± 0.02
m-OCH$_3$	2.70 ± 0.02
m-CH$_3$	1.43 ± 0.02
H	1.00
p-Cl	0.73 ± 0.02
m-Cl	0.31 ± 0.02

[a] Reaction conditions: Substituted arylacetic acid (10 mmol), phenylacetic acid (10 mmol), potassium bis(biuretato)cuprate(III) (2 mmol), glacial acetic acid (10 ml), reflux temperature, reaction period 2 h. [b] Values given are the average of two or three independent experiments, each analyzed twice by GLC.

k_H/k_D value could be calculated, being 2.5 ± 0.2 and 1.0 ± 0.2 for p-xylene and benzene, respectively.

Competition experiments. In order to compare the copper(III) decarboxylation with other metal ion decarboxylations[13] the competitive decarboxylation of a series of substituted arylacetic acids was studied. The relative rates of decarboxylation were determined from the relative amounts of the corresponding benzyl acetates produced under conditions where these acetates accounted for more than 90 % of all products observed (results and reaction conditions, see Table 3). Excluding the rates for the methoxy compounds which appear to be abnormally high, the log k_{rel} were plotted against the substituent constants σ_m and σ_{p+}[15] and gave a ρ value of -1.4 ($r=0.998$). The plot of this correlation is given in Fig. 1. If the same rate data are plotted *vs.* σ_m and σ_p or if the data of the methoxy compounds are included, the correlation is not significant ($r=0.83$ and 0.93, respectively).

DISCUSSION

The reaction between copper(III) and aromatic compounds in acetic acid gave a product pattern characteristic for reactions of other strong oxidants such as the anode,[16] metal ions[13,17] such as iron(III), cobalt(III), manganese(III) and silver(II) and the sulfate radical[14] which presumably all react *via* an electron transfer mechanism.[9] Oxidation of mesitylene and naphthalene in a non-nucleophilic medium gives coupling products which
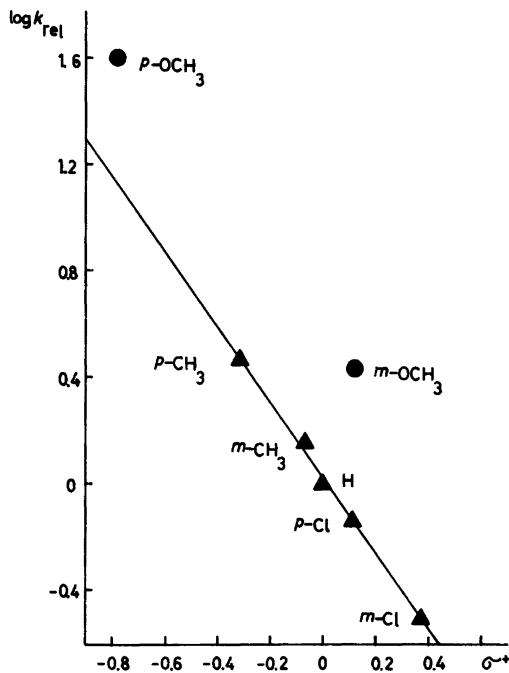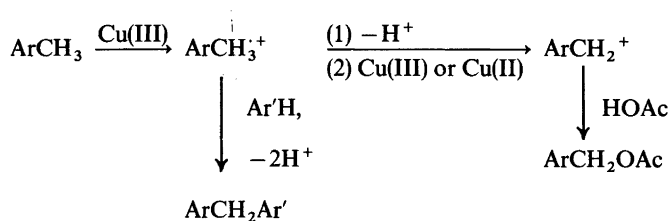

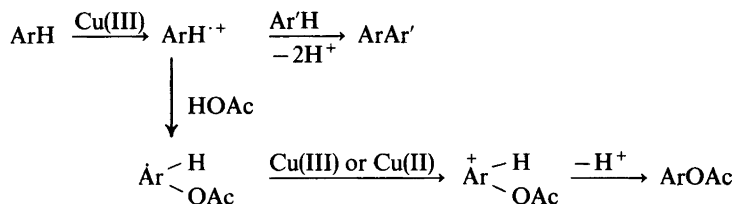*Fig. 1.* Plot of log k_{rel} *vs.* substituent constants.

are also formed by electrochemical oxidation of the same substrates, a process known to proceed *via* a radical cation mechanism.[16] The formation of 1-mesitylnaphthalene can be interpreted in the following way. The oxidation potential of naphthalene is lower than that of mesitylene (1.64 *vs.* 1.85 V)[18] whereas mesitylene is more basic than naphthalene. Consequently naphthalene is oxidized preferentially and the mesitylene reacts with the naphthalene cation radical and gives 1-mesitylnaphthalene. The same interpretation has been given for the electrochemical reaction.[19,20] In the light of these facts the most likely mechanisms for the copper(III) oxidation of aromatic compounds are shown in Schemes 1 and 2.

The observed isotope effects (k_H/k_D 2.5 for side-chain substitution and 1.0 for nuclear substitution) are in accord with this mechanism. These values may be compared to those obtained in the anodic side-chain acetoxylation (k_H/k_D 2.6)[16] and the side-chain acyloxylation by sulfate radical (k_H/k_D 2.2).[14]

The oxidation of p-anisylmercury(II) acetate presumably does not follow an outer-sphere electron transfer mechanism since this compound is very resistent ($E_{\frac{1}{2}} \geq 3.5$ V *vs.* SCE) towards direct oxida-

$$ArCH_3 \xrightarrow{Cu(III)} ArCH_3^{\cdot +} \xrightarrow[\text{(2) Cu(III) or Cu(II)}]{\text{(1) } -H^+} ArCH_2^+$$

$$ArCH_3^{\cdot +} \downarrow Ar'H, \quad ArCH_2^+ \downarrow HOAc$$

$$\downarrow -2H^+ \qquad ArCH_2OAc$$

$$ArCH_2Ar'$$

Scheme 1.

$$ArH \xrightarrow{Cu(III)} ArH^{\cdot +} \xrightarrow[-2H^+]{Ar'H} ArAr'$$

$$\downarrow HOAc$$

$$\overset{H}{\underset{OAc}{Ar{<}}} \xrightarrow{Cu(III) \text{ or } Cu(II)} \overset{+}{Ar}{\overset{H}{\underset{OAc}{<}}} \xrightarrow{-H^+} ArOAc$$
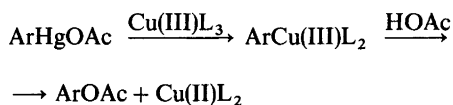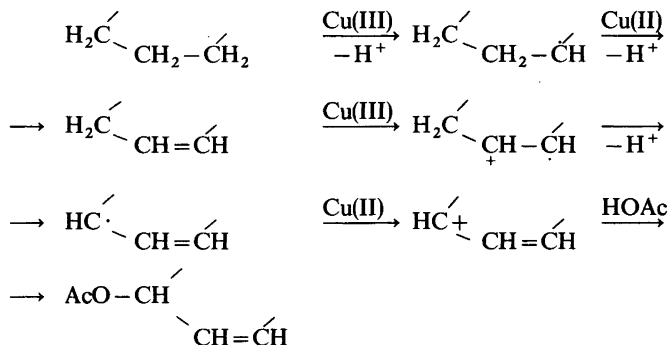
Scheme 2.

tion.[21] The high product selectivity (p-/o-methoxy-phenyl acetate 9:1) make a mechanism involving transmetallation more likely (Scheme 3). The first step is the formation of the corresponding aryl-copper(III) intermediate by metal exchange. The product forming step is a reductive elimination, a reaction also observed for alkylcopper(III) intermediates generated by the addition of alkyl radicals to copper(II) complexes.[22]
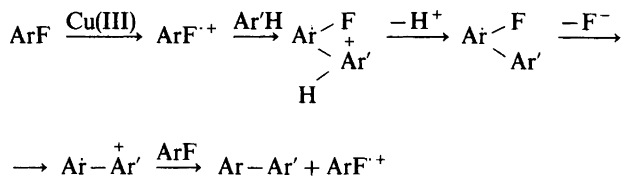
$$ArHgOAc \xrightarrow{Cu(III)L_3} ArCu(III)L_2 \xrightarrow{HOAc}$$

$$\longrightarrow ArOAc + Cu(II)L_2$$

Scheme 3.

Formation of 3-cyclohexenyl acetate from cyclohexane and cyclohexene can be explained by a mechanism analogous to the one operating in the oxidation of cyclohexane by cobalt(III) in the presence of copper(II) ions[23] (Scheme 4). The initial step is an H atom transfer from the C−H bond to a ligand atom of complex 1. This type of H atom transfer has also been suggested as the rate-determining step in the oxidation of aromatic compounds by 12-wolframocobalt(III)ate ion.[24] Electrochemical oxidation of substituted adamantanes has been associated with a radical cation mechanism,[25] whereas oxidation with metal ions has been

$$H_2C{\underset{CH_2-CH_2}{<}} \xrightarrow[-H^+]{Cu(III)} H_2C{\underset{CH_2-CH}{<}} \xrightarrow[-H^+]{Cu(II)}$$

$$\longrightarrow H_2C{\underset{CH=CH}{<}} \xrightarrow[]{Cu(III)} H_2C{\underset{\underset{+}{CH}-CH}{<}} \xrightarrow[-H^+]{}$$

$$\longrightarrow HC{\cdot}{\underset{CH=CH}{<}} \xrightarrow{Cu(II)} HC{+}{\underset{CH=CH}{<}} \xrightarrow{HOAc}$$

$$\longrightarrow AcO-CH{\underset{CH=CH}{<}}$$

Scheme 4.

$$ArF \xrightarrow{Cu(III)} ArF^{\cdot +} \xrightarrow{Ar'H} \underset{H}{\overset{Ar'}{Ar\underset{\searrow}{\overset{F}{\underset{+}{\searrow}}}}} \xrightarrow{-H^+} Ar\overset{F}{\underset{Ar'}{\diagdown}} \xrightarrow{-F^-}$$

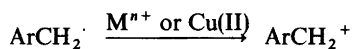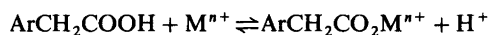$$\longrightarrow Ar\overset{+}{-}Ar' \xrightarrow{ArF} Ar-Ar' + ArF^{\cdot +}$$

Scheme 5.

described as an electrophilic attack at a C−H bond.[13,25] On the basis of the present work it is impossible to assign a definitive mechanism for copper(III) oxidation of adamantane.

The remarkably high yields of the copper(III) initiated hydrolysis of disubstituted aryl halides support our previously suggested electron transfer chain mechanism. However, it has not been possible to obtain catalytic yields of phenols derived from monosubstituted aryl halides, since these phenols are oxidized further very easily. The formation of biphenyls by halogen/aryl exchange can also be described by the electron transfer chain terminology (Scheme 5).

The metal ion promoted decarboxylation of arylacetic acids has been extensively studied.[13] Trahanovsky *et al.* suggested a mechanism involving homolysis of a metal-carboxylate complex for cerium(IV) decarboxylation[26] (Scheme 6, M = Ce(IV)). In this reaction a series of substituted arylacetic acids follows a Hammett correlation with $\rho = -2.9$ $(r=0.97)$, using σ_{p+} substituent constants. Two methoxyphenylacetic acids (*m* and *p*) were exceptions, being oxidized by cerium(IV) at rates that were very high based on expectations derived from the Hammett correlation. For these compounds a process involving electron transfer from the aromatic ring was postulated [Scheme 7, M = Ce(IV)]. On the other hand, a good correlation with $\rho = -2.9$ $(r=0.99)$ including both of these methoxy substituted acids was obtained for cobalt-(III) decarboxylation.[27] In this case a single mechanism involving an electron transfer from the

aromatic ring was suggested (Scheme 7, $M^{n+} =$ Co(III)). It is known that the ρ value for most processes leading to a benzylic radical in the rate-determining step is in the range of -0.3 to -2.9.[26,28-30] Since the ρ value $(\rho = -1.4, r=0.998)$ obtained in the copper(III) oxidation is located in that range it supports the mechanism shown in Scheme 6, $M^{n+} =$ Cu(III), suggested by Trahanovsky *et al.*[26] for cerium(IV) promoted decarboxylation. The rapid rate of copper(III) decarboxylation

$$ArCH_2COOH + M^{n+} \rightleftharpoons ArCH_2CO_2M^{n+} + H^+$$

$$ArCH_2CO_2M^{n+} \longrightarrow ArCH_2^{\cdot} + CO_2 + M^{(n-1)+}$$

$$ArCH_2^{\cdot} \xrightarrow{M^{n+} \text{ or } Cu(II)} ArCH_2^+$$
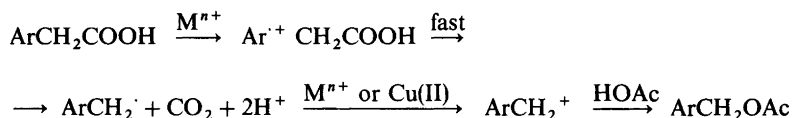
$$\xrightarrow{HOAc} ArCH_2OAc$$

Scheme 6.

of the methoxy substituted acids indicates that these acids are oxidized by a different mechanism, probably involving a radical cation intermediate (Scheme 7).

EXPERIMENTAL

Materials. Potassium bis(biuretato)cuprate(III) and potassium bis(biuretato)nickelate(III) were prepared according to a literature method.[7] Anisylmercury(II) acetate was prepared according to a

$$ArCH_2COOH \xrightarrow{M^{n+}} Ar^{\cdot +} CH_2COOH \xrightarrow{fast}$$

$$\longrightarrow ArCH_2^{\cdot} + CO_2 + 2H^+ \xrightarrow{M^{n+} \text{ or } Cu(II)} ArCH_2^+ \xrightarrow{HOAc} ArCH_2OAc$$

Scheme 7.

known procedure and was recrystallized twice from ethanol – water (50:50) m.p. 176 – 177 °C.[31] All other chemicals used in this investigation were either purchased in the highest quality available or prepared according to known methods described in earlier work.[14,16,19,23,32]

Oxidation procedure. A mixture of the aromatic compound, complex *1* and, in some cases, water, in a solvent (25 ml) was stirred for 2 h at reflux temperature (see also Table 1). 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: 10 mmol of each of two phenylacetic acids were heated at reflux temperature in a mixture of glacial acetic acid (10 ml) and *1* (2 mmol) for 2 h. The work-up procedure was the same as above.

Analysis. Yields and isomer distribution 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 column and a 2 m × 3 mm 3 % OV 101 on Chromosorb Q column. The yield was determined using an internal standard (*m-tert*-butylphenyl acetate, phenyl acetate 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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