Metal Ion Oxidation. IV.\textsuperscript{1} Oxidative Acetoxylation of Arenes by Bis-(2,2′-bipyridine)-silver(II) Peroxysulfate in Acetic Acid

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Organic complexes of silver(II) are known to be strong oxidants.\textsuperscript{8} The stability is dependent on the nature of the ligands as well as the acidity of the medium employed. Some of these complexes have been shown to be effective in the oxidation of carboxylic acids,\textsuperscript{9} alkylarenes \textsuperscript{4\textsuperscript{a}} and alcohols.\textsuperscript{4\textsuperscript{b}} The direct displacement of hydrogen by an acetoxy group in oxidation reactions is of synthetic importance.\textsuperscript{7} We now wish to report a new route to aryl and benzyl acetates using bis-(2,2′-bipyridine)-silver(II) peroxysulfate.\textsuperscript{**} I, in the oxidative acetoxylation of aromatic compounds. When I was stirred with an excess of anisole in glacial acetic acid for 65 h at room temperature the three isomeric acetoxanisoles were formed in 31% yield, based on silver(II). (It is assumed that 2 Ag(II) ions are required to form one molecule of aryl acetate.) However, since the brown color of I had not disappeared the reaction had not gone to completion.

A remarkable effect was observed when the reaction was repeated in the presence of 0.5 M sodium acetate. After 17 h the reaction was complete as indicated by the change in color from brown to yellow. The yield of acetoxanisoles was now 157%. This shows that the peroxysulfate ion must be involved in the overall reaction. In a control experiment it was shown that no reaction occurred when potassium peroxysulfate was employed in the absence of silver(II) or silver(I) ion. We therefore assume that the peroxysulfate ion in I is utilized for reoxidizing silver(I) ions and that every peroxysulfate ion is capable of oxidizing two silver(I) ions.\textsuperscript{10} The latter assumption was borne out by the fact that 4-methoxytoluene was oxidized by I in the presence of sodium acetate yielding 290% of a mixture of 4-methoxybenzyl acetate and 4-methoxybenzaldehyde in a ratio of 76:24. Assuming that 2 Ag(I) ions are oxidized by one peroxysulfate ion the theoretical yield is 300% based of silver(II). Table 1 contains additional data for several compounds.

\begin{table}
\centering
\begin{tabular}{|l|c|c|}
\hline
\textbf{Compound} & \textbf{Reaction time} & \textbf{Yield of ArOAc} \\
 & \textbf{h} & \textbf{\%} \\
\hline
Anisole & 17 & 157 (\(\alpha:\beta = 68:1:31\)) \\
Biphenyl & 22 & 55 (\(\alpha:\beta = 22:78\)) \textsuperscript{b} \\
Naphthalene & 5 & 190 (\(\alpha:\beta = 93:5\)) \\
1,4-Dimethoxybenzene & 2 & 183 \\
Mesitylene & 65 & 42\textsuperscript{c} \\
\hline
\end{tabular}
\caption{Product yields in the Ag(bipy)$_2$S$_4$O$_8$ oxidation of arenes in 0.5 M NaOAc/HOAc based on Ag(II).}
\end{table}

\textsuperscript{a} Complete reaction. \textsuperscript{b} 0.1% meta isomer. \textsuperscript{c} 3,5-Dimethylbenzaldehyde (7%) and 3,5-dimethylbenzyl acetate (18%) were also formed.

The isomer distribution in the silver(II) oxidative acetoxylation of aromatic compounds shown in Table 1 is similar to that obtained in anodic acetoxylation.\textsuperscript{11} If the instability of the acetoxy radical\textsuperscript{12} is also taken into account, it appears safe to conclude that the initial step in the oxidation of aromatic compounds by silver(II) in acetic acid is the transfer of one electron from the aromatic substrate to the silver(II) ion analogously to the corresponding anodic process.\textsuperscript{7} The proposed reaction sequence for the formation of acetoxyarenes in the silver(II) oxidation is shown below. The same mechanism has been suggested

\[
\text{Ag(II)} + \text{ArH} \quad \longrightarrow \quad \text{Ag(I)} + \text{ArH}^+ \\
\text{ArH}^+ + \text{OAc}^- \quad \longrightarrow \quad \text{Ar} \quad \text{OAc} \\
\text{Ag(II)} + \text{Ar} \quad \longrightarrow \quad \text{Ag(I)} + \text{Ar} \quad \text{OAc} \\
\text{Ar} \quad \text{OAc} \quad \longrightarrow \quad \text{ArOAc} + \text{H}^+ \\
2\text{Ag(I)} + S_4O_6^{2-} \quad \longrightarrow \quad 2\text{Ag(II)} + 2 \text{SO}_4^{2-}
\]

for several reactions involving oxidation by metal ions.\textsuperscript{13-19} It has been suggested that in aqueous systems the sulfate anion radical, which is an intermediate in the decomposition of peroxysulfate ions,\textsuperscript{20} reacts with aromatic compounds giving cation radicals.\textsuperscript{21} Although a similar reaction is possible in the acetic acid

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\textsuperscript{** Prepared in the same way as the corresponding pyridine complex; see Palmer, W. G., Ed., \textit{Experimental Inorganic Chemistry}, Cambridge University Press, Cambridge 1965, p. 158.}
system we consider it unlikely, since no acetox-
aromatic compounds were formed when potas-
sium peroxodisulfate was stirred in a mixture of
acetic acid and an aromatic compound even
at elevated temperatures. The effect of sodium
acetate on the reaction rate is probably caused
by its buffer capacity, since protons are
produced in the reaction.

Our assumption that the peroxodisulfate
ion reoxidizes silver(I) ions led us to investigate
the possibility of running the reaction cata-
lytically in silver(II) by using an excess of
peroxodisulfate ion. Thus, when I was stirred
in 0.5 M sodium acetate/acetic acid containing
naphthalene in the presence of an excess of
potassium peroxodisulfate * a mixture of α- and
β-acetoxynaphthalenes in a ratio of 95:5
was obtained in a 2700 % yield based on
silver(II) and a 22 % yield based on peroxo-
sulfate, respectively. A similar oxidation of
4-methoxytoluene produced a mixture of 4-
methoxybenzaldehyde and 4-methoxybenzyl
acetate in a 4000 % yield (21 % based on
peroxodisulfate).

We are currently investigating other silver(II)
complexes than that used in the experiments
described above. The tetrapyridine complex of
silver(II) peroxodisulfate turned out to be
an even stronger oxidant, but its use in acetic
acid is limited due to oxidative decarboxylation
of the solvent. We have also found that it is
possible to acetoxylate aromatic compounds
using silver(I) acetate in the presence of 2,2'-
bipyridine and potassium peroxodisulfate.

Experimental. Compound I was prepared in
the same way as the corresponding tetra-
pyridine complex. Acetic acid was frozen out
twice before use. Other compounds were of
high commercial purity. Reaction mixtures
were analyzed by TLC with a Varian 1400 gas
chromatograph on a 2.5 m x 0.3 cm 5 % UIIPs
on Chromosorb W column or a 3 m x 0.3 cm
10 % APL on Chromosorb P column. The
products were identified by comparison with
authentic samples. Yields were calculated by
integration of the GLC peaks after calibration
of the authentic samples against a standard.

A solution of the aromatic substrate (10 mmol)
and the complex in 20 ml 0.5 M sodium acetate
in acetic acid was stirred at room temperature.
Ether was then added and the salts were
filtered off. The filtrate was washed with water,
dried over anhydrous sodium sulfate and
analyzed by GLC. The results are shown in
Table 1.

In the catalytic oxidations a suspension of
K2S2O8 (10 mmol), I (0.1 mmol), aromatic
substrate (20 mmol), and 40 ml 0.5 M NaOAc/
HAc was stirred at room temperature during
17 h. The reaction mixture was worked up as
above.

* The Ag(II) complex and potassium peroxo-
sulfate are practically insoluble in acetic acid.

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