<table>
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<td>Ichikawa, Katsuhiko; Ouchi, Hajime</td>
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Kyoto University
ABSTRACTS

The Kinetics of the Demercuration Reaction of Benzyl- and \( \beta \)-(p-Methoxyphenyl)-ethyl-mercuric Acetate with Perchloric Acid

Katsuhiko ICHIKAWA and Hajime OUCHI


To clarify the mechanism of the final steps involved in the reactions of olefin-mercuric acetate addition compounds with aromatics to form \( \beta \)-arylethyl acetates (cf. J. Am. Chem. Soc., 80, 6005 (1958); 81, 3401 (1959)), the kinetics of the demercuration reaction of benzyl- and \( \beta \)-(p-methoxyphenyl)-ethyl-mercuric acetate (one of the intermediate mercurials) have been studied. In aqueous acetic acid solutions containing perchloric acid, rate expressions were established for the second-order reaction 1 and first-order reaction 2.

\[
\begin{align*}
\text{ArCH_2HgOAc} + \text{HgOAc}_2 & \quad \text{H}^+ \rightarrow \text{ArCH_2OAc} + \text{Hg_2OAc}_2 \quad 1. \\
\text{ArCH_2HgOAc} & \quad \text{H}^+ \rightarrow \text{ArCH_2OAc} + \text{Hg} \quad 2.
\end{align*}
\]

Perchloric acid concentrations affected the rates of both reactions remarkably. Possible mechanisms are proposed below. For reaction 1,

\[
\begin{align*}
\text{HgZ}_2 + \text{H}^+ & \rightarrow \text{HgZ} + \text{H}_2Z \\
\text{ArCH}_2\text{HgZ} & \quad \text{R.D.} \rightarrow \text{ArCH}_2\text{OAc} + \text{Hg}_2\text{Z}_2 \\
\text{Z}^+ & \quad \text{R.D.} \rightarrow \text{ArCH}_2 + \text{Hg}
\end{align*}
\]

For reaction 2,

\[
\begin{align*}
\text{ArCH}_2\text{HgOAc} + \text{H}^+ & \rightarrow \text{ArCH}_2\text{Hg}^0 + \text{HOAc} \\
\text{ArCH}_2\text{Hg}^0 & \quad \text{R.D.} \rightarrow \text{ArCH}_2 + \text{Hg}
\end{align*}
\]

The Kinetics of the Decompositions of Ethylene-Mercuric Salt Addition Compounds with Hydrochloric Acid

Katsuhiko ICHIKAWA, Hajime OUCHI and Shigemitsu ARAKI

J. Am. Chem. Soc., 82, 3880 (1960)

The kinetics of decompositions of ethylene-mercuric salt addition compounds with hydrochloric acid \((\text{ROCH}_2\text{CH}_2\text{HgCl} + \text{HCl} = \text{CH}_2\text{CH}_2 + \text{HgCl}_2 + \text{ROH})\) has been studied in water-ethanol mixtures and found to be third order (first order in addition compounds, hydronium ion and chloride ion, respectively). Selected values of the kinetic data are shown in the table below.