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FORMATION OF ETHYLENE FROM BETA-HALOPROPIONIC ACIDS.

Manfred K. Eberhardt and Karen Soto, University of Puerto Rico, Medical Sciences Campus, Department of Pathology, G.P.O. Box 5067, San Juan, Puerto Rico, 00936.

Summary: The reaction of beta-halopropionic acids with peroxydisulfate and Ag^+ *in aqueous solutions gives in high yield ethylene via the intermediate formation of beta-haloalkyl radicals and subsequent reductive elimination by* Ag^+.

In a previous publication (1) we have reported the formation of olefins via reductive elimination from beta-substituted alkyl radicals by reducing metal ions (Fe^{2+}, Fe^{2+} - EDTA, Cu^+). In these experiments we obtained these beta-substituted radicals by hydrogen abstraction from alcohols, alkyl acetates, ethers, and alkyl halides. In most of these cases the yield of beta substituted alkyl radicals is small (other abstraction reactions being predominant) and therefore the yield of olefins is small.

Since it is well known that Ag^{2+} reacts with carboxylic acids to give alkyl radicals (2) we have examined the reaction of beta-halopropionic acids with $S_2O_8^{2-}$ and Ag^+ in aqueous solutions. This reaction gives ethylene in high yields. Some typical results are shown in Table I.

The reaction mechanism can be summarized as follows:

$$\begin{array}{lll}
(1) & S_2O_8^{2-} + Ag^+ \longrightarrow Ag^{2+} + SO_4^{-} + SO_4^{2-} & \text{initiation} \\
(2) & ClCH_2CH_2COOH + Ag^{2+} \longrightarrow ClCH_2CH_2COO + H^+ + Ag^+ & \\
(3) & ClCH_2CH_2COO \longrightarrow ClCH_2CH_2 + CO_2 & \text{propagation} \\
(4) & ClCH_2CH_2 + Ag^+ \longrightarrow CH_2 = CH_2 + Cl^- + Ag^{2+} & \\
(5) & Cl^- + Ag^+ \longrightarrow AgCl & \\
\hline
 & ClCH_2CH_2COOH + Ag^+ \longrightarrow CH_2 = CH_2 + CO_2 + H^+ + AgCl &
\end{array}$$

The chain character of the reaction follows from the results in Table I. With 0.25 x 10^{-3} moles of $S_2O_8^{2-}$ we obtain more than 3 times the amount of ethylene. In our previous work (1) we have shown that Fe^{2+} reacts with beta-haloalkyl radicals to give olefins. We have therefore examined the reaction of beta-chloropropionic acid with $S_2O_8^{2-}$ and Fe^{2+} with and without EDTA. In both cases we did observe the formation of only small amounts of ethylene (see Table II). These results are consistent with the observations of Anderson and Kochi (2) that in the Ag^+ - $S_2O_8^{2-}$ system the Ag^{2+} is responsible for most of the decarboxylation. It has indeed been observed by ESR that only a fraction of $SO_4^{-\bullet}$ react with aliphatic acids to give alkyl radicals via decarboxylation, the major reaction being hydrogen abstraction (3).

References:

1. Eberhardt, M. K., J. Org. Chem., 1986, 49, 3720.
2. Anderson, J. M. and Kochi, J. K., J. Am. Chem. Soc., 1970, 92, 1651.
3. Vasudeva, W. C., J. Chem. Soc. Perkin II, 1975, 697.

TABLE I

Reaction conditions[1] (Reactants in moles x 10^3)			Products[2] (in moles x 10^6)
$S_2O_8^{2-}$	Ag^+	time (hrs.)	CH_2=CH_2
2	2	2	844, 817
2	4	2	1205, 1224
2	8	2	1300, 1280
1	2	2	759,842
1	4	2	968, 1073
1	8	2	1033, 1150
0.5	2	1.5	933,918,875
0.5	4	1.5	906, 1000
0.5	4	72	949
0.5	8	1.5	1025, 1114
0.25	2	1.5	613,606,683
0.25	2	72	766
0.25	4	1.5	680, 814, 757
0.25	4	72	813
0.25	8	1.5	780, 890
2*	2	3	431
2*	4	3	675

1) All reactions were carried out in 25 ml aqueous solutions containing 1.84 x 10^{-3} moles of beta-chloropropionic acid in 150 ml bottles with a rubber septum. Argon was bubbled through the solution prior to the addition of $AgNO_3$.
2) The ethylene was analyzed by gas chromatography, using a 6 foot Carbosieve B column (Supelco) at 130°C. Gas mixtures containing known amounts of ethylene were used as standards (Scotty II gas mixtures). The numbers represent results of different experiments.
(*) These last two experiments are with 1.84 x 10^{-3} moles of beta-bromopropionic acid instead of beta-chloropropionic acid.

TABLE II

Reaction conditions[1] (Reactants in moles x 10^3)				
$S_2O_8^{2-}$	Fe^{2+}	EDTA	time (hrs.)	CH_2=CH (moles x 10^6)
2.5	5	0	3	16
2.5	5	1	3	6
2.5	5	0	72	18
2.5	5	1	72	7

1) Reaction conditions were the same as in footnote 1, Table I.

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