

FORMATION OF ETHYLENE FROM BETA-HALOPROPIONIC ACIDS.

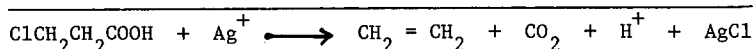
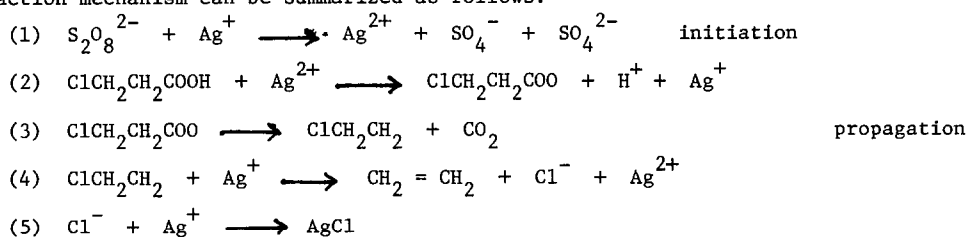
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Summary: The reaction of beta-halopropionic acids with peroxydisulfate and Ag⁺ in aqueous solutions gives in high yield ethylene via the intermediate formation of beta-haloalkyl radicals and subsequent reductive elimination by Ag⁺.

In a previous publication (1) we have reported the formation of olefins via reductive elimination from beta-substituted alkyl radicals by reducing metal ions (Fe²⁺, Fe²⁺ - 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 Ag²⁺ reacts with carboxylic acids to give alkyl radicals (2) we have examined the reaction of beta-halopropionic acids with S₂O₈²⁻ 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:



The chain character of the reaction follows from the results in Table I. With 0.25 x 10⁻³ moles of S₂O₈²⁻ we obtain more than 3 times the amount of ethylene. In our previous work (1) we have shown that Fe²⁺ reacts with beta-haloalkyl radicals to give olefins. We have therefore examined the reaction of beta-chloropropionic acid with S₂O₈²⁻ and Fe²⁺ 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⁺ - S₂O₈²⁻ system the Ag²⁺ is responsible for most of the decarboxylation. It has indeed been observed by ESR that only a fraction of SO₄⁻ 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 ₂ O 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 1.84×10^{-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 AgNO₃.

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 1.84×10^{-3} moles of beta-bromopropionic acid instead of beta-chloropropionic acid.

TABLE II

Reaction conditions ¹ (Reactants in moles x 10 ³)				CH ₂ =CH (moles x 10 ⁶)
S ₂ O ₈ ²⁻	Fe ²⁺	EDTA	time (hrs.)	
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.

(Received in USA 24 April 1987)