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A New Synthesis of Tri- and Tetrachloroethylene from Acetylene and Copper Chlorides

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It is a well known fact that the chlorination of acetylene in a solution containing copper chlorides and hydrogen chloride yields *trans*-1,2-dichloroethylene and 1,1-dichloroethylene.¹ The ratio $\text{Cu}^{2+}:\text{Cu}^+$ to be used in this reaction is 1:4 to 1:9. It is also known that vinyl chloride, monovinylacetylene and other derivatives can be synthesized from acetylene, hydrogen chloride, and cuprous chloride. In all these methods a strongly acidic solution is used.

Surprisingly, it was found that by using a less acidic solution and a high $\text{Cu}^{2+}:\text{Cu}^+$ ratio, tri- and tetrachloroethylenes could be synthesized directly from acetylene in very high yields.

In the first experiments acetylene was pumped through a vertical tube containing a nearly boiling aqueous solution of cupric chloride and lithium chloride. After a few minutes a reaction started and the deep

green solution darkened due to the formation of cuprous chloride complexes. At the same time, tri- and tetrachloroethylene distilled from the top of the tube. The highest reaction rate with respect to trichloroethylene was reached when one fourth to one fifth of the cupric ions were reduced.

In the following experiments the copper chloride solution ($\text{Cu}^{2+}:\text{Cu}^+ = 80:20$) was pumped in from the bottom at the same level as the acetylene and at such a rate that only 1–2 % of the Cu^{2+} was reduced before the solution left the column in the upper part. The conversion of acetylene to chloride compounds was about 90 %, 85 % of which was a mixture of trichloroethylene and tetrachloroethylene.

The factors influencing these reactions have been evaluated and the most important are:

1. $\text{Cu}^{2+}:\text{Cu}^+$ -ratio
2. pH of the solution
3. The total chloride concentration of the solution. More than 10 moles/liter has to be used in order to obtain good complexing of the cuprous chloride. It is well known that alkali chlorides are good agents for these purposes. It was found that chlorides of Li, Mg, Ca, and NH_4 were better than those of Na and K.
4. The copper concentration has to be high in order to get a small reaction tube.

Nothing is exactly known about the mechanism of this reaction, but Bodländer

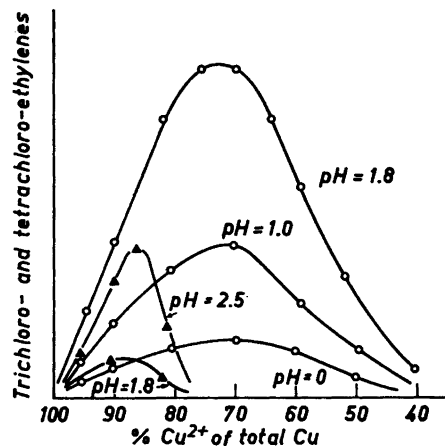
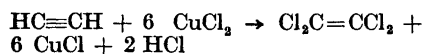
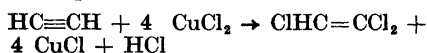


Fig. 1. Effect of $\text{Cu}^{2+}:\text{Cu}^+$ -ratio and pH on the formation of chloroacetylene. O, trichloroacetylene; \blacktriangle , tetrachloroacetylene.

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and Storbeck² assumed that the complex ions in concentrated copper chloride solutions were CuCl_3^{2-} . Later on Szabo³ and Tschaltykjan⁴ showed that in a solution where the mole ratio $\text{CuCl}:\text{MeCl}$ is <0.6 the dominating ions are CuCl_3^{2-} . It may now be assumed that these ions react with acetylene to give for example $\text{Cu}_2\text{ClC}\equiv\text{CH}$ which adds chlorine, or in a more neutral medium behaves as an acid to give the ion $\text{Cu}_2\text{ClC}=\text{C}^-$, which would be the precursor for the formation of tetrachloro ethylene.

The reactions may be summed up in the following formulas:



This new reaction may be used for the industrial production of tri- and tetrachloro ethylene.⁵ Most methods known to-day are using two reaction steps. They also involve great losses of chlorine. An advantage of this new reaction is that cheap hydrogen chloride + oxygen or chlorine may be used for the re-oxidation of cuprous chloride. It is also to be assumed that this new reaction will be suitable for the production of bromoethylenes, or mixed bromo-chloro-ethylenes.

Experimental. A hot (+ 97°C) solution of CuCl_2 (3 moles/liter) and LiCl (6 moles/liter) was continuously pumped in from the bottom of a column (height 100 cm, diameter 5 cm). About 25 % of the Cu^{2+} was pre-reduced to Cu^+ . The pH was about 1.5 (this value was measured with a standard glass electrode on a sample which was diluted with an equal part of distilled water in order to avoid crystallization of CuCl). Acetylene (10 l/h) was pumped in from the bottom and the used chloride solution was withdrawn at the top of the column. There was also a trap for condensing the organic chloro compounds produced. The conversion of acetylene in this experiment was 90 % and the yield of trichloroethylene 80 %. Byproducts were tetrachloroethylene and dichloroethylenes.

Further information about this reaction will be published elsewhere.

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Specific Interaction of Adenine Nucleotides with the Amino Acid Transport Mechanism in the Nuclear Membrane

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The transport of amino acids into isolated calf thymus nuclei has been shown to require the presence of sodium ions. The process is specific for the L-form of the amino acids and has well-defined temperature and pH optima. Amino acids can be divided into groups whose members exhibit mutual competition in transport.¹ Low concentrations of adenine nucleotides in the medium reduce the transport by about 40 %.² The phenomenon has been further characterized and the inhibition found to be a specific property of adenine nucleotides. The transport mechanisms for L-alanine and L-arginine are inhibited to the same degree, whereas the diffusion of the amino acids remains unaffected.

Transport was measured by incubating the isolated nuclei with the ¹⁴C-labelled compound and measuring the radioactivity in the acid-extract of the nuclei after washing them free of external isotope. The incubation time used was 10 min. The time for equilibration of the labelled compounds was over 20 minutes in all cases, so the values measured represent transport rates.

When nuclei were incubated with different nucleoside triphosphates, ATP reduced the transport of L-alanine by 38 % (Table 1, Expt. 1). Of the corresponding monophosphates only AMP was found to have the same effect (Table 1, Expt. 2). ATP, ADP, and AMP were inhibitory whilst