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STUDY OF THE ELECTROCHEMICAL CHLORINATION OF ACETONE

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Riche [1] and Shrer [2] have reported that the electrochemical chlorination of acetone in hydrochloric acid gives CH_3COCH_2Cl (I). The yield of (I) on a platinum anode in a diaphragmless electrolyzer or on a graphite anode in a diaphragm electrolyzer is close to quantitative [2]. At pH above 7, the electrochemical chlorination of acetone leads to $CHCl_3$ as a result of haloform cleavage [3, 4]. However, these data and the results of Tomilov [5] and Tedoradze [6] are in disagreement with more recent findings on the chlorination of acetone [7, 8].

In a voltamperometric study, we showed that acetone is electrochemically inactive under electrochlorination conditions both in acid and weakly basic media. Thus, the formation of chloro derivatives is the result not of electrode reactions, but rather subsequent bulk reactions.

In reproducing the results of Shrer [2], we found that a mixture of (I), 1,1- (II), and 1,3-dichloroacetone (III) is formed under the conditions studied, i.e., at 22-25°C in concentrated hydrochloric acid upon passing 50% of the theoretical current. The overall current yields were 78% on graphite and 79% on platinum.

Studies showed that the ratio of (I) and the dichloro derivatives may be controlled by the amount of current passed per mole substrate. A decrease in the acid concentration reduces the rate of the side reactions but the mixture of (II) in (I) is not less than 5-8% even in the case of a 5-7-fold excess of acetone.

Since the rate of the haloform cleavage of the trihaloketones is a function of the OH ion concentration, we may propose that the major product of the chlorination of acetone at pH ≈ 7 will be CH_3COCCl_3 (IV), and not $CHCl_3$. However, our attempts to obtain (IV) starting from acetone under these conditions proved unsuccessful. Only traces of (I) and (II) and a small amount of $CHCl_3$ were found in the organic phase. On the other hand, we found that the selective formation of (IV) without significant haloform cleavage proceeds upon the electrochemical chlorination of (I) or (II) in a diaphragm electrolyzer in the presence of an equivalent amount of $NaHCO_3$, which is in accord with patent data on the chlorination of these compounds with concurrent treatment by solutions of NaClO and phosphoric acid [8].

The difference in the results of the electrochemical chlorination of acetone and its chloro derivatives may be attributed to hydrolysis and chlorination processes. In the chlorination of acetone, intermediate (I) enters further transformations at the instant of its formation in the homogeneous medium in the fully hydrated form, while (I) when used as the starting compound is present predominantly as an emulsion. This situation is even more pertinent to (II), which is less soluble in water.

EXPERIMENTAL

The identification of the products of the chlorination of acetone and analysis of the composition of the reaction mixtures was carried out by PMR spectroscopy on a Tesla BS-467 spectrometer at 60 MHz with TMS as the internal standard in CCl_4 and by gas-liquid chromatography on an LKhM-80 chromatograph using a 3 m × 3 mm column packed with 5% SE-30 on Chromatone N-AW-DMCS (0.16-0.3 mm).

Electrochemical Chlorination of Acetone in Concentrated Hydrochloric Acid [2]. A sample of 200 ml concentrated hydrochloric acid and 82 ml (1.1 moles) acetone were placed into a di-

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aphragmless electrolyzer equipped with a stirrer, thermometer, reflux condenser, and platinum electrodes with 45 cm^2 working surface each. A current of 4.5 A (equivalent to 1 F/mole) was passed at 22-25°C and vigorous stirring. After electrolysis, the reaction mixture was stirred for an additional 30 min, neutralized with $CaCO_3$ to pH 7, and extracted with four 200-ml portions of CH_2Cl_2 until the red color is no longer observed upon making the aqueous and organic phases basic. The extract was dried over Na_2SO_4 and the solvent was distilled off to give 41.1 g of a light yellow mixture, containing (I), (II), (III), and condensation products in 74:18.5:5.6:1.9 mole ratio. Distillation gave 34.7 g of a fraction with bp 118-120°C which is a 75:25 mixture of (I) and (II). The current yield relative to (I) was 67%. Analogous results were obtained upon carrying out the reaction in concentrated hydrochloric acid according to Shrer [2] in a diaphragmless electrolyzer on graphite electrodes.

Electrochemical Chlorination of Acetone in 20% Hydrochloric Acid. A sample of 500 ml 20% hydrochloric acid and 183 ml (2.5 moles) acetone were placed into the electrolyzer described above. A current of 4 A (0.4 F/mole) was passed at 23-25°C and vigorous stirring. The products were separated by the above procedure to give 42.13 g of a mixture of products containing (I), (II), and (III) in 92:6.5:1.5 mole ratio. Distillation gave 40.1 g of a mixture containing 92% (I) and 8% (II). The current yield was 87% relative to (I).

Electrochemical Chlorination of (I) in Carbonate Buffer Solution. An anolyte consisting of a solution of 47 g $NaHCO_3$ and 64 g NaCl in 230 ml water and 11.25 g (0.12 mole) (I) and a catholyte consisting of 60 ml sat. aq. NaCl were introduced into an electrolyzer with a ceramic diaphragm equipped with a 100-cm^2 ruthenium oxide–titanium oxide anode and a 40-cm^2 graphite cathode. A current of 11 A (5 F/mole) was passed with vigorous stirring at 23-25°C. The organic layer was separated. The aqueous layer was extracted by three 100-ml portions of CH_2Cl_2. The extracts were combined with the organic layer and dried over Na_2SO_4. Distillation gave 16.1 g (82%) (IV), bp 133-135°C [9].

Analogously, 31.4 g (0.25 mole) (II) upon passing 2.2 F/mole gave 27.5 g of a mixture containing 30% (II) and 70% (IV), which corresponded to 65% conversion of (II).

CONCLUSIONS

1. The electrochemical chlorination of acetone in aqueous hydrochloric acid leads to a mixture of mono- and dichloro derivatives, the ratio of which is a function of the current passed.

2. The electrochemical chlorination of monochloroacetone and 1,1-dichloroacetone in carbonate buffer solution leads to 1,1,1-trichloroacetone in good yield.

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