AN ELECTROCHEMICAL METHOD OF PRODUCTION OF SODIUM 2,3-DIBROMOPROPANESULFONATE IN UNITHIOL MANUFACTURE

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The industrial production of unithiol (IV) occurs in aqueous medium without the isolation of intermediate products, according to the scheme

$$CH_{2} = CH - CH_{2}Br + Na_{2}SO_{3} \rightarrow CH_{2} = CH - CH_{2}SO_{3}Na + NaBr$$
I
I
(A)

$$CH_{2} = CH - CH_{2}SO_{3}Na + Br_{2} \rightarrow CH_{2}BrCHBrCH_{2}SO_{3}Na$$
II
III
(B)

$$\begin{array}{c} CH_{2}BrCHBrCH_{2}SO_{3}Na + 2KSH \rightarrow HSCH_{2}CH(SH)CH_{2}SO_{3}Na + 2KBr \\ III & IV \end{array} \tag{C}$$

From the scheme cited it is evident that in the process of conversion of allyl bromide (I) to IV, three moles of bromide salts are formed. In the purification of IV through the lead complex (V) (1), the mother liquors containing the indicated bromide salts are discarded into the sewage system. The production of elementary bromine from them can be accomplished by the well-known methods used in bromine production [2].

However, we undertook to produce sodium 2,3-dibromopropanesulfonate (III) without the use of liquid bromine. For this purpose we investigated the electrochemical bromination of sodium allylsulfonate (II). Such a method of bromination permits the use of sodium bromide, isolated according to Eq. A, in the process, and, consequently, an almost twofold reduction of the bromine consumption. In addition, work with liquid bromine is excluded, which substantially improves the conditions of work on production.

Electrochemical bromination of II occurs as a result of two successive reactions: the anodic oxidation of bromide ions to elementary bromine $2 \operatorname{Br}^- 2e \rightarrow \operatorname{Br}_2$ and the interaction of bromine "at the moment of liberation" with II. The limiting step of the process is the oxidation of bromide ions.

The experiments were conducted in a glass electrolyzer equipped with a mixer. The cathodic space (iron cathode) was separated from the anodic space (carbon anode) by a porous ceramic partition. A solution of II was loaded into the anodic space and dry sodium bromide added to it in an amount such that the mole ratio of sodium bromide and II was 2.05:1. A 5% solution of sodium bromide was loaded into the cathodic space.

It was established that at the indicated reagent ratio, the yield of III depends substantially on the current density and on the temperature. The electrochemical bromination of II was studied at the temperature $28-30^{\circ}$ and an anodic current density of 0.1, 0.07, and 0.055 A/cm²; in this case the yield of III was 67, 82, and 93%, respectively. The dependence of the yield of III on the temperature was studied at a current density of 0.055 A/cm². It was found that when the temperature is raised to 50°, the yield of III decreases to 65%, evidently on account of the occurrence of side processes of oxidation of II.

From the data obtained it follows that the best conditions for the electrochemical bromination of Π are an anodic current density of 0.055 A/cm², temperature 28-30°, and excess of sodium bromide 0.05 mole per mole of II. The proposed method of electrochemical bromination of Π permits the elimination of the

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• 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00. use of liquid bromine from the production, and also a simplification of the regeneration of bromine from the waste products of the step of production of V, since bromine can be isolated in the form of bromide salts.

EXPERIMENTAL

Sodium 2,3-Dibromopropanesulfonate (III). To 360 g of the reaction solution, containing 72 g (0.5 mole) II and 51 g sodium bromide, we added 57 g of dry sodium bromide, 36 ml of water, and placed the solution in the anodic space of the electrolyzer. We loaded 350 ml of a 5% solution of sodium bromide into the cathodic space. The mother liquor from the step of production of the lead complex V, containing potassium bromide, can be used as the catholyte. Electrolysis is conducted at a current density of 0.055 A/cm^2 and a temperature of 28-30° for 15 h. After the end of the bromination the reaction mass contains 141 g III (yield 93% of the theoretical). The yield of III was calculated by determining the content of organically bound bromine in solution.

The product obtained was treated with a 50% solution of potassium hydrosulfide, and V was precipitated from the IV obtained by the action of a 40% solution of lead acetate. The yield and qualtiy of V corresponded to the requirements of the industrial regulation.

LITERATURE CITED

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