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Comparatıve Chlorınatıon Of C_3 -C_4 OLEFİNS By A Electrochemical Method

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Abstract
In researches the process of electrochemical chlorination of propylene in hydrochloric acid, graphite anodes, diaphragm electrolysis device has been developed. At a concentration of 5 – 10% hydrochloric acid, at a temperature of 35 - 50 ^{0}C, at a current density of 5-10 A/dm^2 , the current yield of PXH is 95-97% and the selectivity is 85-87%.
In the electrochemical chlorination of isobutylene in a hydrochloric acid medium, 1-chlorine-2-methylpropanol-2 and 1.3-dichloro-2-methylpropanol-2 are obtained in a ratio of 7:3, respectively. In a 15% acidic environment, at a current density of 20 A / dm 2 and at a temperature of 30.0 C, the current yield of chloride is 93.5%. The process of chloridation of C_3 -C_4 hydrocarbonsin hydrochloric acid medium was determined on the basis of anode polarization curves. Chlorhydrins are mainly formed by the interaction of olefins with electrochemically generated chlorine in the electrolyte volume.
Keywords: hydrochloric acid, electrochemical chlorination, propylene chloride, 1-chlorine-2-methylpropanol-2, 1.3-dichloro-2-methylpropanol-2, graphite anode, electrolysis.

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I. Introduction

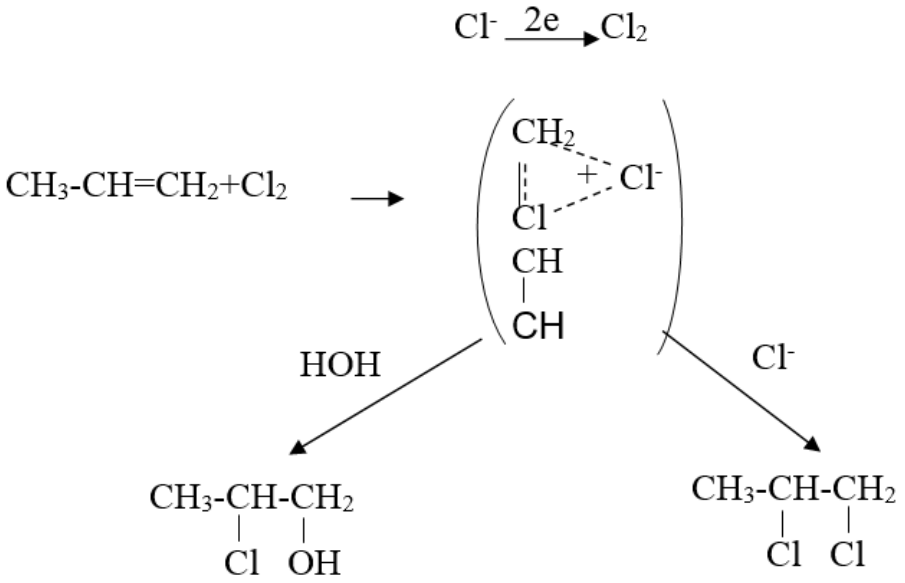
Oxides obtained from chlorinated hydrogens by the chlorinated method are one of the multi-ton solutions of the chemical industry, such as propylene glycol, polyester resins, emulsifiers, polyurethane foam, antifreezes, surfactants, etc. Used as a main product in the purchase. Oxides derived from chlorhydrins are used as lubricants and hydraulic fluids due to their low freezing point and high viscosity. At the same time, the field of application of these oxides is expanding. Therefore, research in the field of electrochemical chlorination to increase or improve the production capacity of these oxides is more relevant [1].

C_3 -C_4 hydrochlorides are also obtained on the basis of 2.0-2.5% hydrochloric acid and a large amount of 1,2,3-trichloropropane obtained as a stoichiometric intermediate in the process of chlorination of epichlorohydrin . The method of obtaining 3-dichloroacetone was studied. The regularities of the process were studied, and in order to achieve the main goal, the following were solved in the research work: obtaining chlorine from hydrochloric acid by electrolysis and using it in the production of dichlorohydrin glycerin; use of background electrolytes in order to make maximum use of hydrochloric acid in the production of dichlorohydrin glycerin, obtaining and thickening of chloride solution in the presence of background electrolytes at the expense of 3-5 *% hydrochloric acid in dichlorohydrin glycerin solution;* Study of the regularity of the process of obtaining 1,3-dichloroacetone in the presence of oxidants in hydrochloric acid of 2,3-dichloropropen-1, a product of dehydrogenation of 1,2,3-trichloropropane, and by electrolysis; Development of a basic technological scheme of the process of thickening of a solution of dichlorohydrin glycerol at the expense of hydrochloric acid, which is an intermediate product in the process of obtaining glycerol dichlorohydrin by chlorine method.

II. Results and discussion

The synthesis of chloride by electrochemical chlorination of hydrocarbons C_3 -C_4 in hydrochloric acid was studied under the influence of various factors in a 250 ml diaphragm glass laboratory electrolyzer using platinum, graphite and MEDIUM anodes [2, 3].

Chlorine formed in the electrolysis of hydrochloric acid interacts with C_3 -C_4 hydrocarbons that continuously enter the aqueous medium of the electrolyzer at the moment of formation and forms the product of chlorhydrination according to the following scheme:



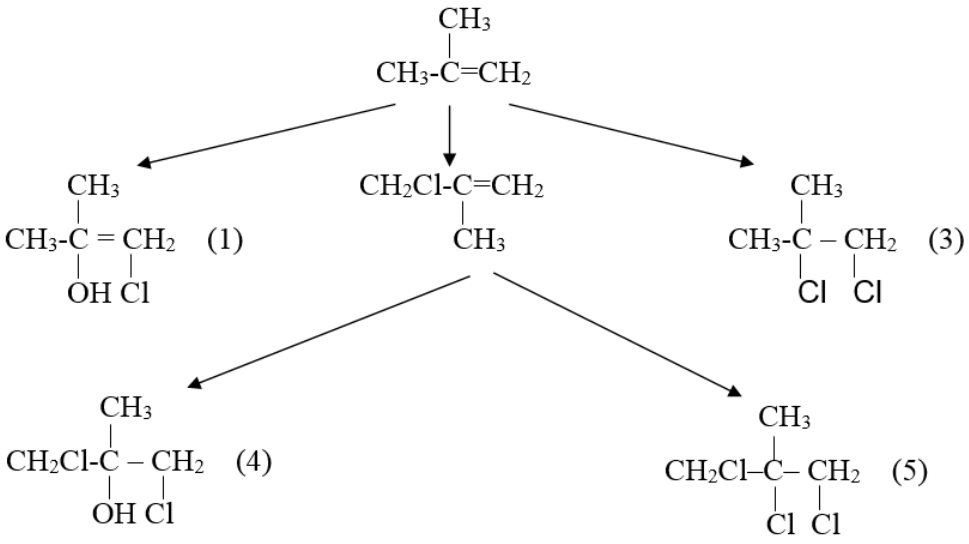
Researches showed that in the electrochemical chlorination of propylene, only two aqueous and organic layers are formed, as in the reaction of chemical chlorination of olefins with hydrochloric acid and hydrogen peroxide.

It should be noted that the ratio of the yield of the resulting reaction products depends largely on the conditions of synthesis.

C_3-C_4 chlorhydrins in the electrochemical system, the effect of hydrochloric acid concentration, current density, temperature, concentrations of hydrochlorides in the electrolyte and the nature of the electrodes were studied.

C_3-C_4 In the continuation of research in the field of electrochemical chlorination, as well as to determine the simplicity of the reaction, isobutylene chlorination was carried out in a glass laboratory electrolyzer under the above method under the synthesis of propylene chloride [4].

In the electrochemical chlorination of isobutylene in the presence of hydrochloric acid, along with 1-chlorine-2-methylpropanol-2, as well as 1-chlorine-2-methylpropene, 1,2-dichloro-2-methylpropane, 1,3-dichloro -2-methylpropanol-2 and 1.2.3 - The probability of formation of trichlor-2-methylpropane occurs according to the following scheme.



Under the conditions of electrolysis of hydrochloric acid, there is some need to study the regularities of the chlorination of olefins. Of particular importance is the study of the chlorination of propylene and the adsorption of products on electrodes.

The chlorination reaction of propylene was studied in the presence of electrodes platinum [5, 6], ORTA [7, 8], and a lot of evidence was obtained about its mechanism when a graphite electrode was taken.

We assume that the reaction at the graphite [anode]takes place in two stages: the electrochemical generation of chlorine and the interaction with propylene with a greater volume of electrolyte. A two-chamber reactor (Figure 1) is used to verify this probability, where the electrolysis of a solution containing HCl and dissolved chlorine is carried out first, and the second C_3-C_4 hydrocarbons (or *propylene*) are injected into the bubbling stage. The results of the experiments are given in Table 1. Evidence from the table shows that the PXH yield obtained in a two-chamber reactor is slightly lower than the results obtained in a single-chamber reactor, which is either due to the loss of free chlorine or the involvement of the electrode in surface processes.

III. Experimental part

It is known that the separation of chlorine in graphite takes place in three successive stages by a combined mechanism [9].

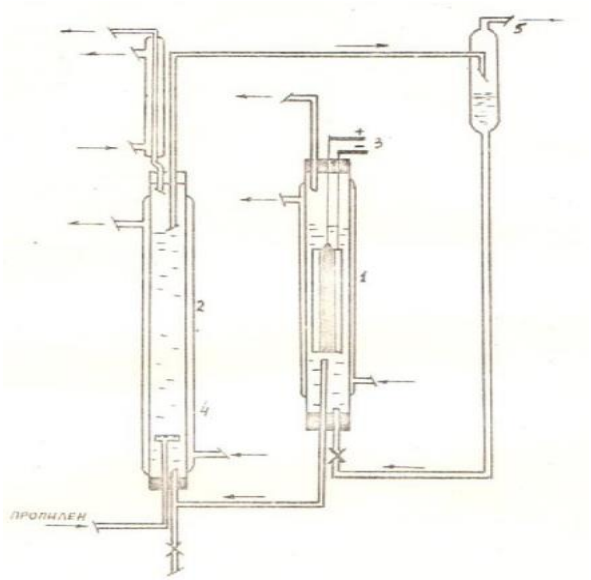


Figure 1. Chlorination of C_3-C_4 hydrocarbons with a circulating electrolyte .
1 - electrolysis of HCl, 2 - delivery of propylene, 3 - electrodes, 4 - filter, 5 - pump.

Table 1
Chlorhydrination of propylene under the conditions of electrolysis of hydrochloric acid in a two-chamber reactor.

(t - 35 - 50 ^{0}C, U - 2.2-3.2 v)

Concentration of HCl,%	i_a, A / cm ^{2}	Electrolyte volume, ml	Q, A ·clock	Purchased PXH		Current output of PXH,%	Note
				q	%		
5	0.05	750	2.6	5.9	0.38	64.0	Circulation with UR-3 thermostat
5	0.1	350	5.2	5.4	1.5	59.5	Rashig rings have also been placed in the second reactor
10	0.1	240	5.6	7.1	2.8	71.5	It is circulated by a water pump
10	0.1	250	6.0	8.4	3.8	80.0	Single-chamber reactor, without circulation

$$Cl^- - e \longrightarrow Cl_{ads}$$
$$Cl_{ads} - e \longrightarrow Cl^+$$
$$Cl^+ + Cl^- \longrightarrow Cl_2$$

In this case , the chlorination reaction of olefin by interaction with Cl_{ads} or Cl^+ plays an important role. The presence of water is important for the formation of chloride. Therefore, the reaction of chloride formation takes place in the presence of molecular chlorine in the volume of the electrolyte.

Optimal conditions for electrochemical chlorination of isobutylene have been determined in order to carry out the chloridation reaction in the desired direction. For this purpose, the effect of various factors, including the concentration of hydrochloric acid, anode current density and electrolyte temperature, the duration of the electrolysis process, the voltage at the electrodes during the electrolysis process on this reaction was studied.

Studies [10, 11] have shown that the concentration of hydrochloric acid has a significant effect on the yield of the main product. Thus, when the concentration of HCl varies from 5% to 30%, the current output of chloride changes sharply and reaches 48-72%. The higher yield of chloride is 72%, which corresponds to a chlorhydrination reaction with 15% hydrochloric acid at a temperature of 35 ^{0}C and a current density of 10 A / dm ^{2} (table 2).In this case, the delivery rate of isobutylene is 1.5 l / h, the power consumption is 6 A ·h, and the voltage is 2.8 - 3.2 V.

Table 2

Effect of HCl concentration on the yield of isobutylene chloride in a glass laboratory electrolyzer t - 35 ^{0}C, i_a - 10 A/dm^2 , Q - 6 A·hours, U - 2.8-3.2 v.

Concentration of HCl,%	Obtained chloride		Exit according to the current		Yield of chloride in isobutylene,%
	q	%	chloride	dichlorides	
5	6.0	2.9	48.0	1.8	94.5
10	6.3	3.1	51.6	1.8	94.0
15	8.7	3.4	72.2	1.9	93.0
20	7.2	3.1	59.0	3.7	90.0
25	6.4	2.2	53.0	10.8	84.0
30	4.5	1.8	48.0	10.0	80.0

Thus, as a result of research, it was determined that olefins are formed mainly by the interaction of electrochemically generated chlorine in the volume of the electrolyte with the formation of chlorhydrins.

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XÜLASƏ

C₃-C₄ OLEFİNLƏRİN ELEKTROKİMYƏVİ ÜSULLA MÜQAYİSƏLİ XLORLAŞMASI

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Tədqiqatlar xlorid turşusu mühitində, qrafit anodlarda, diafraqmasız elektroliz qurğusunda propilenin elektrokimyəvi xlorhidrinləşdirmə prosesi işlənmişdir. Xlorid turşusunun 5–10 % qatılığında, 35 – 50 ^{0}C temperaturda, 5-10 A/dm^2 cərəyan sıxlığında PXH-nin cərəyana görə çıxımı 95-97 % selektivliyi isə 85-87 % təşkil edir.

Xlorid turşusu mühitində izobutilenin elektrokimyəvi xlorhidrinləşdirilməsində 1-xlor-2-metilpropanol-2 və 1.3-dixlor-2-metilpropanol-2 uyğun olaraq 7:3 nisbətində alınır. 15 %-li turşu mühitində, 20 A/dm^2 cərəyan sıxlığında və 30 ^{0}C temperaturda xlorhidrinin cərəyana görə çıxımı 93.5 %-dir. Xlorid turşusu mühitində C₃-C₄ karbohidrogenlərinin xlorhidrinləşdirmə prosesi anod polyarlaşma əyriləri əsasında təyin edilmişdir. Olefinlərin elektrokimyəvi generasiya olunmuş xlorla elektrolitin həcmində qarşılıqlı təsiri yolu ilə əsasən xlorhidrinlər əmələ gəlir.

Açar sözlər: xlorid turşusu, elektrokimyəvi xlorhidrinləşdirmə, propilenxlorhidrin, 1-xlor-2-metilpropanol-2, 1.3-dixlor-2-metilpropanol-2, qrafit anod, elektroliz.

РЕЗЮМЕ

УДК 541.135.2:547

СРАВНИТЕЛЬНОЕ ЭЛЕКТРОХИМИЧЕСКОЕ ХЛОРИРОВАНИЕ ОЛЕФИНОВ C₃-C₄

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При исследованиях был использован процесс электрохимического хлоргидрирования C₃-C₄ в бездиафрагменной электролизной установке на графитовых анодах в среде соляной кислоты.

При концентрации соляной кислоты 5-10 %, температуре 35-50 ^{0}C, плотности тока 5-10 А/дм^2 выход ПХГ по току составил 95-97 %, а селективность - 85-87%.

При электрохимическом хлоргидрировании изобутилена в среде соляной кислоты получают 1-хлор-2-метилпропанол-2 и 1,3-дихлор-2-метилпропанол-2 в соотношении 7:3. В 15%-ной кислой среде при плотности тока 20 А/дм^2 и температуре 30 ^{0}C выход хлоргидрина по току составляет 93,5%. Процесс хлоргидрирования углеводородов C₃-C₄ в среде соляной кислоты определяли по анодным поляризационным кривым. Было установлено, что хлоргидрины в основном образуются при взаимодействии олефинов с электрохимически генерируемым хлором в объеме электролита.

Ключевые слова: соляная кислота, электрохимическое хлоргидринирование, пропиленхлоргидрин, 1-хлор-2-метилпропанол-2, 1,3-дихлор-2-метилпропанол-2, графитовый анод, электролиз.