Kinetics of Quaternary Ammonium Salts Synthesis

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Abstract: The aim of this work is to study the synthesis of quaternary ammonium compounds based on olefins and to investigate the structure and properties of the obtained products. To achieve this goal, at the first stage, the process of obtaining isohexyl monochloroacetate by the esterification reaction of hexene isomers with monochloroacetic acid in the presence of an acid catalyst was studied and then by the cauterization reaction of the obtained product with triethylamine, quaternary ammonium salts were obtained in an organic solvent medium at 30 °C. The influence of the initial reagents, the nature of the solvent and temperature on the rate of the quaternization reaction was studied. The influence of the reaction duration on the yield of the formed quaternary salts was also studied. The physical properties of the synthesized esters and quaternary ammonium salts were determined. The structure of the product was determined by IR spectroscopy and thermoanalytical methods. A basic technological scheme for the synthesis of quaternary ammonium compounds is proposed.

1 INTRODUCTION

At present, quaternary ammonium salts (QASs) attract the attention of many researchers and scientists around the world. Quaternary ammonium salts are odorless, colorless, characterized by a moderately broad spectrum of antimicrobial activity, residual bacteriostatic effect on treated surfaces, have corrosive activity, efficiency in a wide pH range, resistance to high temperatures, low toxicity [1]. In the recent years, the phenomena of penicillin-resistant bacteria such as methicillin-resistant Staphylococcus aureus (MRSA), or even the emerging of SARS-CoV-2, revived the urgent in development of QASs again [2], [3]. Quaternary ammonium compound (QAC) with positively charged N atom and long-chain alkyl, exhibits efficient antibacterial functions [4]-[6]. The industrial production of quaternary ammonium compounds continues to maintain a leading position due to their steadily growing demand. They are used as target products, feedstock and intermediate products in various chemical and petrochemical synthesis, in the production of composite materials for various fields of chemistry and petrochemistry, in the plastics industry, synthetic resins, electronics, metalworking and chemical-pharmaceutical industries, for the needs of agriculture, farming and production of household chemicals [7], [8]. These productions in many countries of the world are large-, medium- and small-tonnage, as well as diverse in terms of the range of marketable products produced [9]. Therefore, investigating the properties, mechanisms of action, structural characteristics and environmental impacts of quaternary ammonium salts represents a crucial scientific endeavor that integrates both fundamental and applied dimensions of chemistry, biology and ecology. In order to expand the base of starting materials for obtaining functionally substituted ammonium compounds, we have synthesized quaternary ammonium salts. This paper presents the results of the synthesis and study of quaternary ammonium compounds based on hexene isomers. The process of obtaining quaternary ammonium compounds consists of two stages: at the first stage, the reaction of esterification of higher olefins with monochloroacetic acid occurs and at the second stage, the reaction of quaternization of the synthesized isoalkylmonochloroacetates with triethylamine [10].

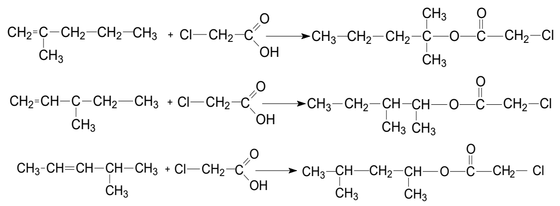
2 METHODOLOGY

The objects of the study are hexene isomers, monochloroacetic acid, triethylamine. The reliability of the research results is confirmed by IR spectroscopy, elemental analysis and thermal analytical studies. The IR spectra of the ester and synthesized copolymers were recorded using a Fourier transform IR spectrophotometer. Infrared Fourier spectrometer "IRTracer-100" (SHIMADZU CORP., Japan, 2017) complete with an attenuated total internal reflection (ATR) attachment MIRacle-10 with a diamond/ZnSe prism (spectral range on the wavenumber scale - 4000÷400 cm^{-1}; resolution - 4 cm^{-1}, sensitivity signal-to-noise ratio - 60,000:1; scanning speed - 20 spectra per second). A DTG-60 series (Shimadzu, Japan) device was used to record thermogravimetric and differential thermal analyses. Over a broad range of DTA measurements, the device's high-precision scales, sensitive detectors and consistent oven temperature distribution enable it to record changes in sample mass up to 1000 mg with an accuracy of 0.1 µg. Gas Flow: 80 [ml/min] in an argon atmosphere, DTA: ±1000 µV.

3 RESULTS AND DISCUSSION

3.1 Synthesis and Kinetic Study of Quaternary Ammonium Salts

The esterification reaction of hexene isomers with monochloroacetic acid (MCAA) in the presence of a catalyst can be described by the following equations:



The reactions were carried out in a solvent medium in the presence of an acid catalyst. Concentrated sulfuric acid was used as a catalyst. The process was carried out with constant stirring and heating of the reaction mixture to temperatures of 40–60°C with condensation of the reactant vapors by means of a reflux condenser. After completion of the reaction, the catalyst was separated by treatment with a 10% alkali solution and the mixture was subjected to vacuum distillation. The synthesized esters are colorless liquids; highly soluble in organic solvents such as acetone, toluene, isopropyl alcohol, diethyl ether, carbon tetrachloride. The optimal reaction conditions were determined, that is, the influence of the nature of olefins, the nature of the solvent, the ratio of the initial reagents and the amount of catalyst on the ester yield was studied.

Benzene, dimethylformamide (DMFA) and 1,4-dioxane were used to study the influence of the nature of the solvent for the reaction (Fig. 1).

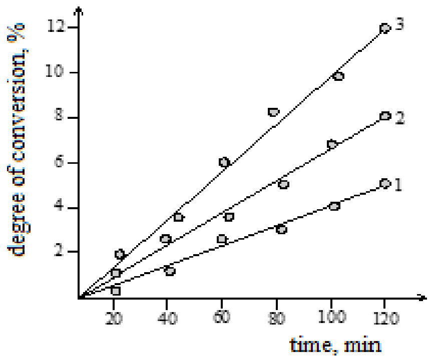


Figure 1: Influence of the nature of the solvent on the ester yield during the esterification of 2-methyl-1-pentene with monochloroacetic acid: 1-benzene; 2-1,4-dioxane; 3-DMFA; t=60 °C.

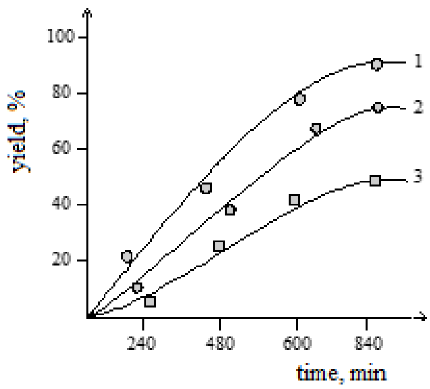


Figure 2: Effect of olefin nature on ester yield: (1) 2-methylpentene-1; (2) 3-methylpentene-1; (3) 4-methylpentene-2, T=60 °C.

As can be seen, with an increase in the dielectric constant of the solvent, the reaction rate and the degree of ester conversion increase and the highest reaction rate is observed in DMFA (Fig. 1).

When studying the influence of the nature of olefins on the ester yield, 2-methylpentene-1, 3-methylpentene-1 and 4-methylpentene-2 were used as initial reagents in the experiments (Fig. 2).

Graphical dependences of the values of the degree of conversion and total rates on the nature of hexenes are shown in Figure 2. They are linear in nature and the highest rate and the product yield is observed during the esterification of 2-methyl-1-pentene with monochloroacetic acid (MCAA).

The data obtained from the study of the effect of temperature and the ratio of the initial reagents on the ester yield show that an increase in the reaction temperature and olefin concentration leads to an increase in the ether yield, the highest yield is observed when the process temperature rises to 60 °C and the ratio of olefin to MCAA = 3:1.

IR spectroscopy methods were used to establish the structure of the starting substances and the products obtained. In the IR spectra of the synthesized esters of isohexylmonochloroacetates, there are absorption bands in the regions: $\nu_{(C=O)}$=1683-1714 cm^{-1}; $\nu_{(C\text{-}O\text{-}C)}$=1256 cm^{-1}; $\nu_{(C\text{-}Cl)}$=661 cm^{-1} (Fig. 3).

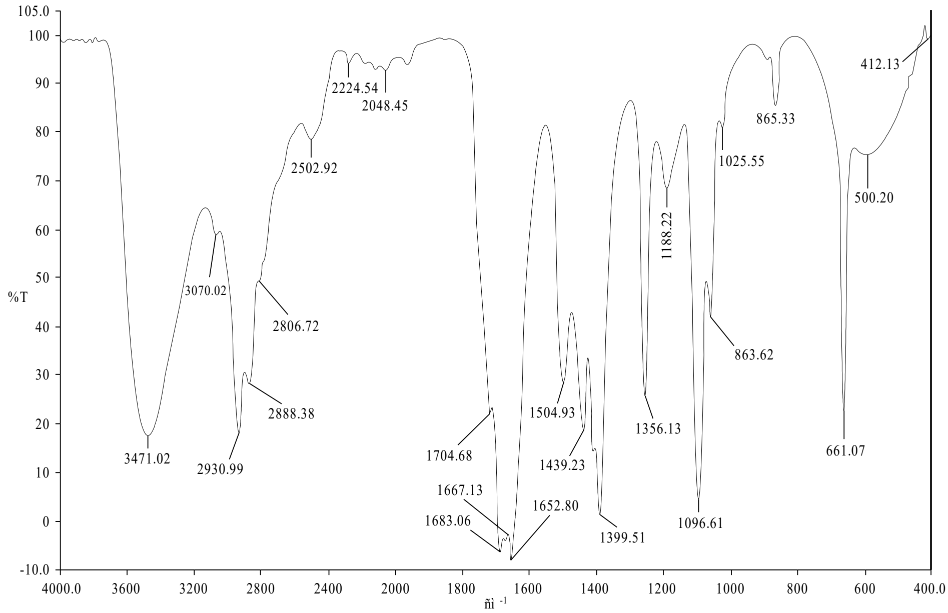


Figure 3: IR spectrum of isohexylmonochloroacetate based on 2-methyl-1-pentene with monochloroacetate.

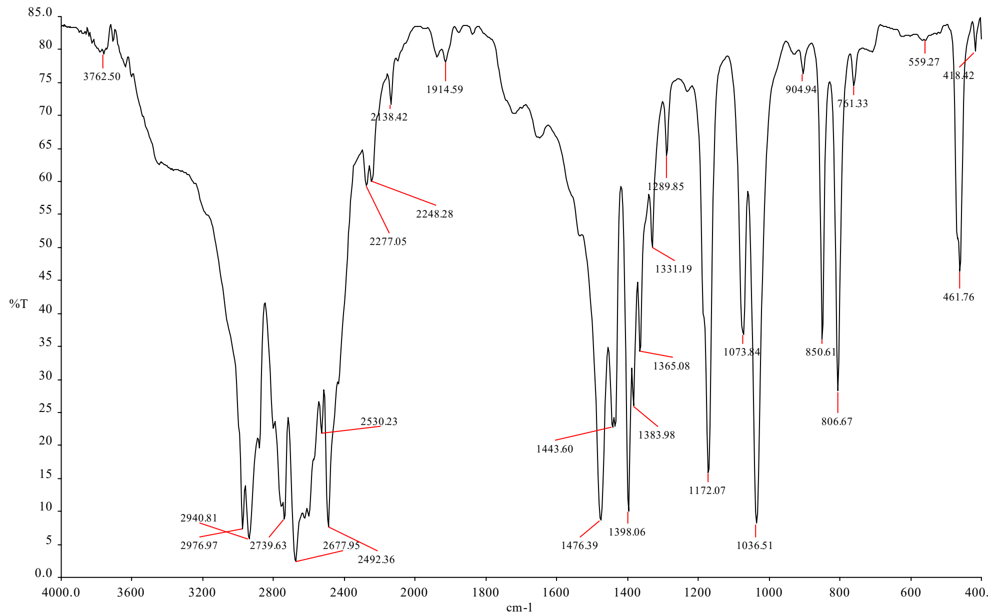
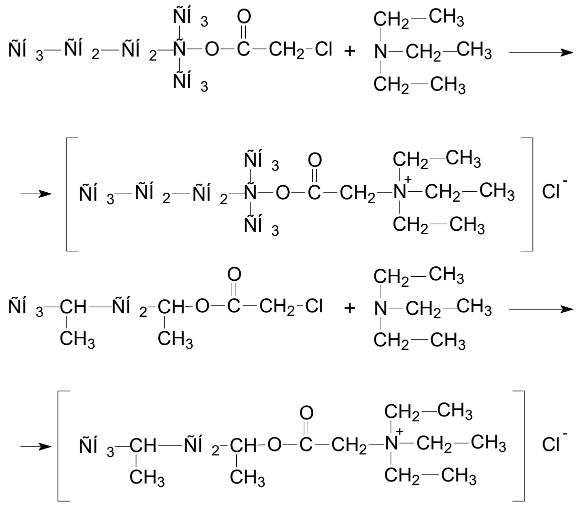


Figure 4: IR spectrum of the quaternary salt of isohexylmonochloroacetate with triethylamine.

At the second stage of the synthesis of quaternary ammonium salts, isohexylmonochloroacetates (IHMClA) were used as an alkylating agent in the quaternization reaction with trimethylamine (TEA). The reactions of their synthesis can be represented as follows:



The structure of the synthesized quaternary salts was proved by the data of IR spectroscopy and elemental analysis. In the IR spectra of QAS, the appearance of an absorption band in the region of 2976–2940 cm^{-1} is observed, which indicates the presence of salt formation, while absorption bands in the region of 1398–1476 cm^{-1} are characteristic of bending vibrations of methylene groups combined with ammonium nitrogen (Fig. 4).

The synthesized ammonium quaternary salts are soluble in water, acetone, benzene, dimethylformamide, slightly soluble in 1,4-dioxane, do not dissolve in diethyl ether.

In this work, we studied the influence of various factors: temperature, the ratio of initial reagents and the duration of the reaction on the QAS yield. The results of experimental studies on the effect of reaction temperature on the QAS yield are shown in Figure 5.

The results obtained show a directly proportional dependence of the product yields on the process temperature, that the maximum QAS yields are observed at 30 °C.

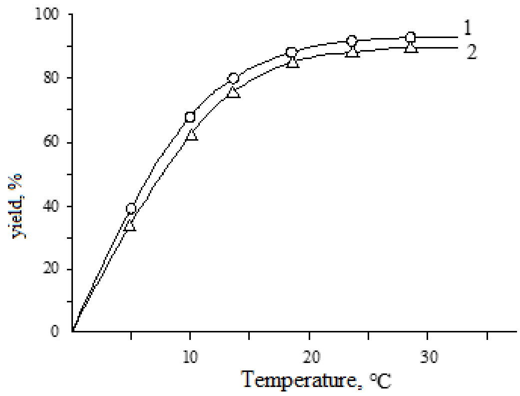


Figure 5: Effect of temperature on the yield QAS: 1– IHMClA:TEA=1.0:1.2; 2– IHMClA:TEA=1.0:1.2; in mass, reaction time 4 hours.

It can be seen from the figure that the rate of the reaction under study increases with increasing temperature and a further increase in temperature does not affect the yield of the product.

Next, the influence of the reaction duration on the yield of the formed QAS was studied (Fig. 6).

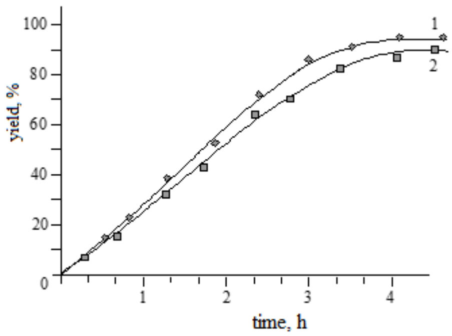


Figure 6: Influence of the reaction time on the yield HOURS (30 °C): 1- IHMClA:TEA = 1.0:1.2, 2- IHMClA:TEA = 1.0:1.2, in mass.

From the graphs showing the dependence of QAC yields on the duration of the reaction, it follows that the interaction of isohexylmonochloroacetate with triethylamine is carried out in 4 hours.

The kinetic orders of the quaternization reaction of isohexylmonochloroacetate with triethylamine were determined (Fig. 7 and 8).

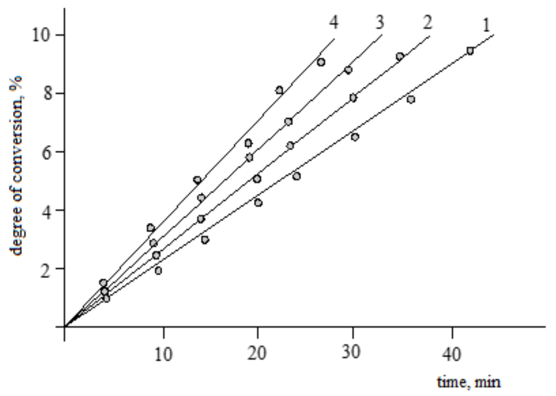


Figure 7: Dependence of the quaternization rate of [IHMClA]: [TEA] on the concentration of TEA; [IHMClA]=1,0 mol/l: [TEA], mol/l: 1-1,0; 2-1,25; 3-1,5; 4-2,0; T=30 °C. The solvent is DMFA.

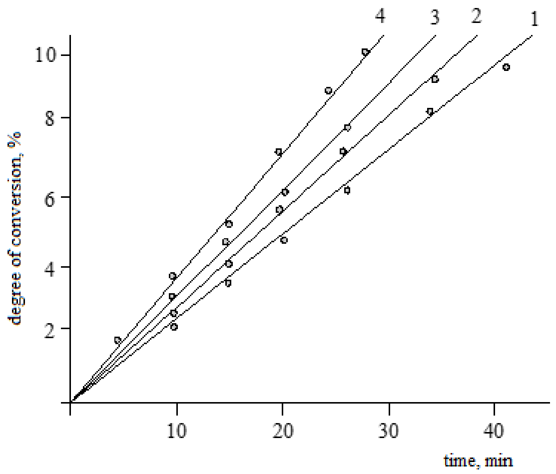


Figure 8: Dependence of the quaternization rate of [IHMClA]: [TEA] on the concentration of IHMClA; [TEA]=1.0 mol/l; [IHMClA], mol/l: 1-1.0; 2-1.25; 3-1.5; 4-2.0. The solvent is DMFA; T=30 °C.

As can be seen from Figures 7 and 8, with an increase in the concentration of the initial reagents, the rate of the quaternization reaction increases.

To determine the order of the reaction, we conducted experiments on the dependence of the rate of the quaternization reaction on the concentration of the initial components (Fig. 9).

The results obtained from Figure 9 also show that the reaction is characterized by the second order in terms of the concentration of the initial components.

Based on the experimental data obtained and according to certain laws of the Menshutkin reaction, the rate of this reaction can be written by the following equation:

$$V_M = \frac{dx}{dt} = K_M * x * y,$$

where, K_M – Menshchutkin reaction constants; x- initial concentration of TEA; y - initial concentration of IHMClA.

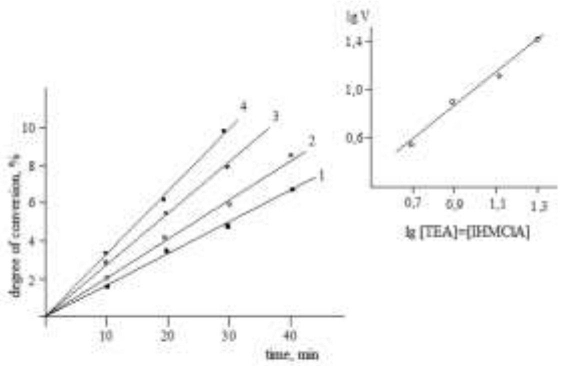


Figure 9: Dependence of the quaternization rate in the TEA-IHMClA system on the concentration of the initial components; [TEA]=[IHMClA], mol/l: 0.5 (1); 1.0 (2); 1.5 (3); 2.0(4). T=30 °C; The solvent is DMFA.

As can be seen, the x-value of the reaction is characterized by the second order.

The value of the Menshutkin reaction rate constant for various temperatures was determined Table 1.

Table 1: Rate constants of the Menshutkin reaction in the TEA-IHMClA system in DMFA at different temperatures.

T, ^{0}C	Initial ratio of components, mol/l		V_M*10^6 mol/l *s	K_M*10^6
	TEA	IHMClA		
20	1,0	1,0	0,61	0,26
20	1,25	1,25	0,96	0,37
20	1,5	1,5	1,22	0,56
20	2,0	2,0	1,65	0,50
30	1,0	1,0	0,45	1,64
30	1,25	1,25	1,20	1,14
30	1,5	1,5	2,42	1,06
30	2,0	2,0	3,5	0,90

Investigation of the effect of temperature on the yield of quaternary ammonium salts, that with an increase in the temperature of the quaternization reaction, the yield of QAS increases and reaches its maximum value of 95% at a temperature of 30 °C.

The value of the Menshutkin reaction rate in the temperature range 10-30 °C was used to calculate the activation energy of the Menshutkin reaction for the [TEA]=[IHMClA] system, which is 61.5 kJ/mol.

Further, thermoanalytical studies of the synthesized quaternary salts were carried out (Fig. 10, 11 and 12).

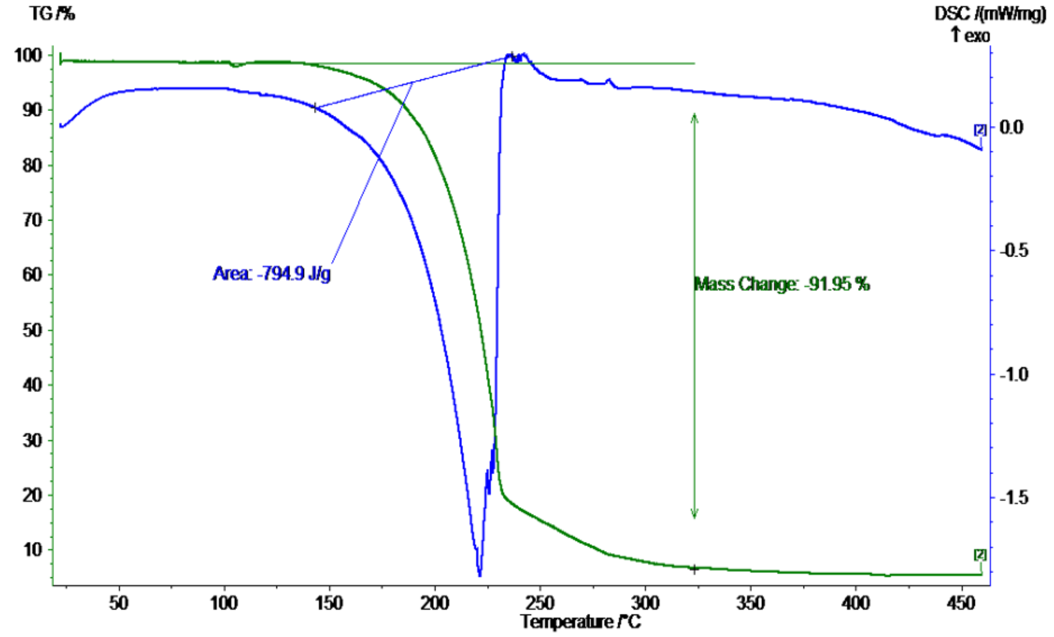


Figure 10: Thermogram of a quaternary salt based on trimethylamine with isohexylmonochloroacetate (1-sample).

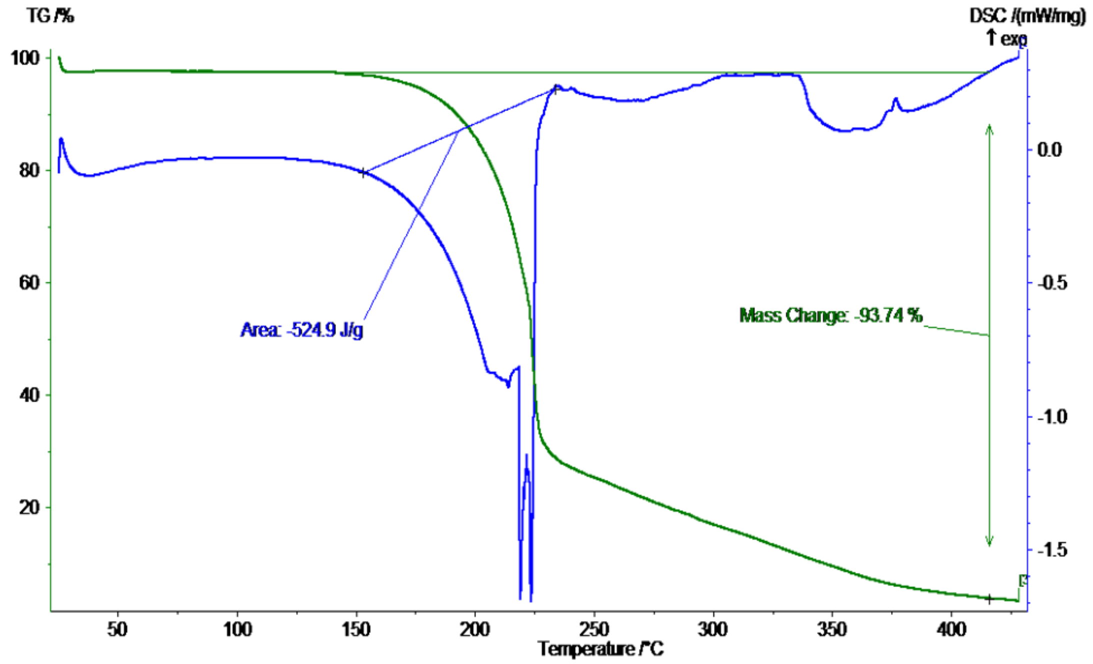


Figure 11: Thermogram of a quaternary salt based on trimethylamine with 3-methyl-pentylmonochloroacetate (2-sample).

As can be seen from the thermograms, endothermic peaks are observed at 220-240 °C. The synthesized quaternary salts are stable up to a temperature of 160 °C. At a temperature of 160 °C, melting occurs, followed by decomposition of the sample. In the temperature range of 160-250 °C, sample 1 loses weight up to 91.9%, sample 2 93.7% and sample 3 80.5%. The corresponding endothermic peaks have a max at 220-230 °C. This weight loss apparently corresponds to the release of volatile components CO_2, NH_3, HCl, H_2O.

Thus, quaternary ammonium salts were synthesized in two steps based on triethylamine and isohexylmonochloroacetate. The effect of the nature of the solvent, temperature and ratio of the initial reagents on the rate of the quaternization reaction and the yield of the product were determined.

3.2 Principal Technological Scheme for the Production of Quaternary Ammonium Salts

As a result of the studies described above, a basic technological scheme for the synthesis of quaternary ammonium compounds was proposed (Fig. 12).

The synthesis of quaternary ammonium salts consists of the following stages:

1) preparation and loading of initial reagents (olefin, monochloroacetic acid, solvent and catalyst);
2) esterification of the olefin with monochloroacetic acid;
3) purification and separation of reaction products;
4) quaternization reaction of the resulting isoalkylmonochloroacetates with triethylamine;
5) filtration, washing and drying of quaternary salts.

The synthesis of isohexylmonochloroacetates is carried out in the reactor 1, equipped with a stirrer jacket, fittings for loading reagents. The calculated amount of olefin, dimethylformamide, monochloroacetate and catalyst is loaded into the reactor 1 and mixing is carried out. The esterification process is carried out with constant stirring at 60 °C for 8 hours. After the end of the reaction, the stirring is stopped and the resulting product is fed into the stripping column 2, where the olefin and dimethylformamide are distilled off at atmospheric pressure. Pairs of olefin and DMF are condensed in the condenser 3 and enter the receivers 4.5, respectively. The olefin and dimethylformamide are returned to the esterification stage, the reaction product isohexylmonochloroacetate through an intermediate vessel 6 and a pump 7 is fed into the jacketed reactor 8. Triethylamine, a solvent, is also supplied there. At the same time, white needle-shaped crystals begin to fall out. The reaction is carried out at 300C for 4 hours. At the end of the process, the reaction mass is passed through a filter 9, where a solid precipitate is separated from it and fed to a film evaporator 10. In the evaporator, the solvent boils off, which, after condensation, is recycled for quaternization. The remaining white crystals are sent for washing with acetone in apparatus 11 and a vacuum evaporator 12 is fed. Ready-made quaternary ammonium salts are sent for packaging.

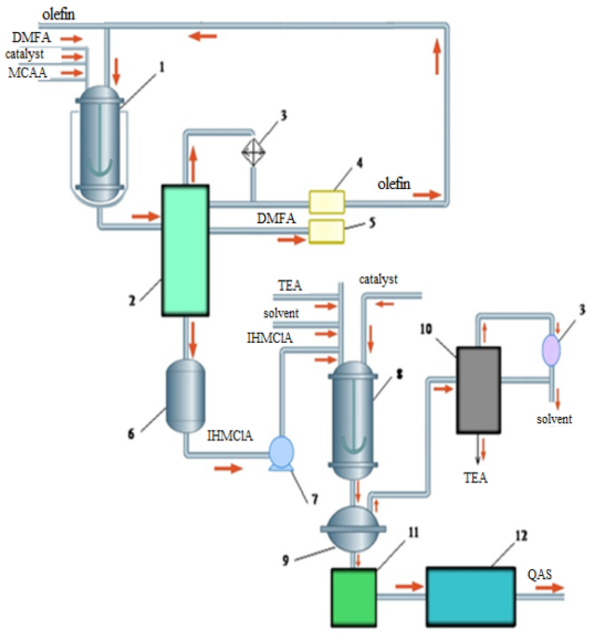


Figure 12: Principal technological scheme for the production of Quaternary ammonium salt: 1,8-reactors; 2-distilling column; 3-water condenser; 4.5 receivers; 6-intermediate capacity; 7-pump; 9-filter; 10-distillation column; 11-washing apparatus; 12-vacuum evaporator.

4 CONCLUSIONS

Based on the conducted research, the following results were obtained:

1) Quaternary ammonium salts were synthesized in two stages: in the first stage, the process of obtaining isohexyl monochloroacetate by the esterification reaction of hexene isomers with monochloroacetic acid in the presence of an acid catalyst was studied and then quaternary

ammonium salts were obtained by the quaternization reaction of the resulting product with triethylamine. The structure of the synthesized quaternary salts was identified using IR spectroscopy and Thermal analysis studies were also conducted.
2) The influence of the nature of the solvent, temperature and the ratio of the initial reagents on the rate of the quaternization reaction and the yield of the product was determined.
3) The kinetic features (reaction orders, reaction rates, reaction rate constants) of the reaction were determined.
4) A basic technological scheme for the production of quaternary ammonium salt is proposed.

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