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SYNTHESIS OF OXYGEN-CONTAINING ORGANIC COMPOUNDS VIA TELOMERIZATION OF LOWER OLEFINS IN THE PRESENCE OF ALIPHATIC ALCOHOLS

Sh.H.Shakarov[1], J.U.Abdullayev[2], S.E.Nurmanov[2], A.E.Ziyadullayev[1], A.Ikramov[1]
[1]Tashkent Institute of Chemical Technology, [2]National University of Uzbekistan
E-mail: imshahzod@gmail.com

Abstract: *In this study, a reaction system involving hydrogen peroxide and acetone was selected to investigate the possibility of obtaining other types of alcohols from lower olefins and aliphatic alcohols. Experiments were carried out at temperatures of 60–100 °C under various pressure conditions, and the resulting mixtures were analyzed by gas chromatography–mass spectrometry (GC–MS). In the preliminary analysis, cyclohexanol- and methylphenol-related mass-spectral features were observed, and their possible formation mechanisms were examined. In these experiments, attention was focused on evaluating the diversity of oxygen-containing organic compounds in the reaction mixture of ethylene and ethanol, particularly on distinguishing components with cyclic structures from other products.*

Keywords: *ethylene, ethanol, hydrogen peroxide, acetone, oxygen-containing organic compounds, cyclohexanol, methylphenol, alcohol synthesis, telomerization, GC–MS.*

QUYI OLEFINLARNING ALIFATIK SPIRTLAR ISHTIROKIDA TELOMERLANISHI ORQALI KISLOROD SAQLOVCHI ORGANIK BIRIKMALAR SINTEZI

Annotatsiya: *Ushbu tadqiqotda quyi olefinlar va alifatik spirtlardan boshqa turdagi spirtlarni olish imkoniyatini o‘rganish uchun vodorod peroksid va aseton ishtirokidagi reaksiya tizimi tanlandi. Tajribalar 60–100 °C haroratda va turli bosim sharoitlarida olib borildi, hosil bo‘lgan aralashmalar gaz xromatografiyasi-mass-spektrometriya (GX-MS) usulida tahlil qilindi. Dastlabki tahlilda siklogeksanol va metilfenolga xos mass-spektral belgilar qayd etildi va ularning hosil bo‘lish mexanizmlari ko‘rib chiqildi. Tajribalarda etilen va etanol reaksiya aralashmasidagi kislorod saqlovchi organik birikmalarning xilma-xilligini baholashga, xususan, siklik tuzilishga ega komponentlarni boshqa mahsulotlardan ajratishga e’tibor qaratildi.*

Kalit so‘zlar: *etilen, etanol, vodorod peroksid, aseton, kislorod saqlovchi organik birikmalar, siklogeksanol, metilfenol, spirtlar sintezi, telomerlanish, GX-MS.*

СИНТЕЗ КИСЛОРОДСОДЕРЖАЩИХ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ ПУТЁМ ТЕЛОМЕРИЗАЦИИ НИЗШИХ ОЛЕФИНОВ В ПРИСУТСТВИИ АЛИФАТИЧЕСКИХ СПИРТОВ

Аннотация: *В данном исследовании для изучения возможности получения иных типов спиртов из низших олефинов и алифатических спиртов была выбрана реакционная система с участием пероксида водорода и ацетона. Эксперименты проводились при температурах 60–100 °C в различных условиях давления, а полученные смеси анализировались методом газовой хроматографии-масс-спектрометрии (ГХ-МС). При предварительном анализе были отмечены масс-спектральные признаки, характерные для циклогексанола и метилфенола, и рассмотрены возможные механизмы их образования. В экспериментах основное внимание уделялось оценке разнообразия кислородсодержащих органических соединений в реакционной смеси этилена и этанола, в частности разделению компонентов с циклическим строением от остальных продуктов.*

Ключевые слова: *этилен, этанол, пероксид водорода, ацетон, кислородсодержащие органические соединения, циклогексанол, метилфенол, синтез спиртов, теломеризация, ГХ-МС.*

1.Introduction

The interaction of unsaturated hydrocarbons with alcohols is one of the important approaches in organic synthesis for extending carbon chains and obtaining oxygen-containing compounds. In such reactions, the product composition largely depends on the nature of the starting materials, the catalytic system, and the reaction conditions. In particular, the telomerization of conjugated dienes with alcohols involves the coupling of hydrocarbon fragments and the participation of alcohols in the reaction, resulting in the formation of new carbon–carbon and carbon–oxygen bonds [1, 2]. Therefore, when describing the telomerization process, it is necessary to consider not only the product yield but also its structure and the ratio of isomers.

The scientific potential of telomerization has been extensively investigated in palladium-based catalytic systems. Researchers led by R. Jackstell demonstrated the formation of alkyloctadienyl ethers in the reaction of 1,3-butadiene with aliphatic alcohols using palladium–carbene complexes. As a result of optimizing the catalyst composition, the turnover number in certain experiments reached up to 1,500,000 [1]. However, high catalytic activity does not always ensure high selectivity toward the desired product. In this regard, Tschan M.J.-L. and other researchers investigated the telomerization

of 1,3-butadiene with methanol. Palladium complexes containing phosphine ligands increased the selectivity toward the formation of 1-methoxyocta-2,7-diene [2]. These results demonstrate that the spatial structure of catalyst ligands plays a decisive role in product distribution.

In addition to catalytic activity, catalyst stability and reusability are also of considerable importance. In the telomerization of isoprene with methanol, the regioselectivity of the products was investigated using a palladium catalyst immobilized on a polymer resin. In particular, the predominance of products of the «tail-to-tail» type was observed, although the catalytic activity decreased upon repeated use [3]. This result demonstrates the need to evaluate the initial efficiency and long-term stability of a catalytic system separately.

In telomerization, the structure of the oxygen-containing starting reagent also influences the direction of product formation. Palio L. and co-authors investigated the reactions of 1,3-butadiene with aromatic hydroxyl-containing compounds in the presence of palladium–N-heterocyclic carbene (Pd–NHC) complexes. The effects of catalyst structure, base nature, and Pd/ligand ratio were studied, and the reactivity characteristics of various phenol derivatives were compared [4]. Since phenols were used as starting reagents, these results cannot be interpreted as evidence of the direct formation of aromatic products from aliphatic alcohols.

The possibility of using other metal catalysts in telomerization reactions has also been investigated. Wang X.-Y. and his research group carried out the arylative telomerization of isoprene using a nickel catalyst and synthesized products with different structures depending on the type of aryl group. High selectivity was achieved in the presence of monophosphine ligands, and the roles of the Ni(0) catalyst and organoboron reagents in the reaction mechanism were demonstrated [5].

This study confirms the possibility of changing the direction of product formation through other catalytic approaches; however, its mechanism differs from classical telomerization with alcohols.

The studies reviewed above demonstrate that catalyst composition, ligand structure, and the properties of starting reagents are important factors determining the product composition in reactions involving unsaturated hydrocarbons [1–5]. However, these studies were mainly carried out using conjugated dienes, such as 1,3-butadiene and isoprene. Ethylene, on the other hand, contains only one double bond, and its reactions in an ethanol medium cannot be directly equated with the catalytic mechanisms described for dienes. Therefore, under conditions where a palladium catalyst is not used, it is necessary to independently analyze the composition of organic components formed in the reaction mixture.

In the present study, the reactions of ethylene in an ethanol medium in the presence of hydrogen peroxide and acetone were investigated. The mixtures obtained at different temperatures and pressures were analyzed by gas chromatography–mass spectrometry (GC–MS), with particular attention paid to the compositional characteristics of oxygen-containing components. The aim of the study was to evaluate the organic compounds identified in the ethylene–ethanol system based on GC–MS results, determine differences between product compositions under different experimental conditions, and scientifically discuss observations related to cyclic oxygen-containing compounds.

2. Research Materials and Methods

In the experiments, ethylene (C_2H_4) and ethyl alcohol (C_2H_5OH), hydrogen peroxide (H_2O_2), and acetone (CH_3COCH_3) were selected as starting materials. Ethylene was selected as the main hydrocarbon feedstock, while ethanol was used as a component forming the liquid reaction medium and participating in chemical interactions. Hydrogen peroxide was used considering its oxidizing properties and its ability to generate reactive radicals under certain conditions, while acetone was used considering its properties as an organic solvent. The reaction system was investigated under conditions without the use of palladium or other metal catalysts.

The experiments were carried out in a laboratory reactor designed for operation under high pressure and equipped with a mechanical stirrer. Ethanol, hydrogen peroxide, and acetone were initially introduced into the reactor, followed by ethylene gas. The required pressure in the reaction system was provided by the ethylene gas itself. During the experiments, stirring was applied to improve contact between the gas and liquid phases and ensure the distribution of reagents throughout the reaction medium. The temperature was controlled using an external heating system, and the reaction was continued under the specified experimental conditions.

In the experiments, temperature, pressure, and reaction duration were selected as the main variable factors. The temperature was varied within the range of 60–100 °C, while the pressure was determined by the amount of ethylene introduced into the reactor in individual experiments. This approach made it possible to compare the composition of product mixtures obtained under different conditions and to identify characteristics associated with changes in temperature and pressure. The experimental conditions are presented in Table 1.

Table 1. Experimental conditions for studying ethylene reactions in an ethanol medium

Experiment	Temperature, °C	Pressure, atm.	Reaction duration, h
1	60	18–24	8
2	80	30–32	6
3	80–85	38–40	4–5
4	100	30	5

At the end of the reactions, the resulting liquid mixtures were analyzed by gas chromatography–mass spectrometry (GC–MS). Using this method, volatile organic components in the mixtures were separated, and their mass-spectral

characteristics were evaluated. The peaks recorded in the chromatograms were compared with the corresponding mass-spectral data. In component identification, molecular ions, characteristic fragment ions, and spectral library data were taken into account. This approach was used for the preliminary evaluation of organic compounds with similar properties in complex mixtures.

Based on the obtained chromatographic data, the compositions of components recorded in different experiments were compared. The relative percentages of peak areas were used to characterize the compositional features of the mixtures. However, their values were not equated with the absolute concentrations or chemical yields of the products. Compounds suggested through mass-spectral library matching were evaluated on the basis of the available analytical evidence, while components requiring additional confirmation of their identification were considered separately. These analytical results formed the basis for discussing the composition and specific characteristics of oxygen-containing organic compounds observed in the ethylene–ethanol system under different conditions.

3. Results and Discussion

The liquid mixtures obtained from the reactions of ethylene in an ethanol medium in the presence of hydrogen peroxide and acetone were analyzed by GC–MS. The experiments were evaluated separately according to temperature, pressure, and reaction duration, with particular attention paid to the identification of individual components, chromatographic peak areas, and mass-spectral identification data. The available results for the main oxygen-containing components are summarized in

Table 2. Selected oxygen-containing organic compounds identified by GC–MS under different experimental conditions

Temperature, °C	Pressure, atm.	Ethyl acetate, %	1,1-Diethoxyethane, %
60	18–24	3.05	13.94
80	30–32	—	—
80–85	38–40	7.82	16.72
100	30	5.86	21.88

***Note**: The values represent the relative percentages of peak areas reported in the GC–MS analyses; they do not indicate product yields or chemical reaction yields. A dash indicates that a sufficiently confirmed value was not available for inclusion in this table.*

In the mixture obtained at 60 °C and 18–24 atm, chromatographic peaks corresponding to ethyl acetate and 1,1-diethoxyethane were recorded. Their relative peak areas were 3.05 and 13.94 %, respectively. In addition, a peak corresponding to diethoxymethane was observed with a relative area of 0.56 %. These results indicate the presence of several oxygen-containing organic components in the reaction mixture in addition to the starting ethanol. However, the mass-spectral composition of the final mixture alone is insufficient to determine the exact pathways through which these compounds were formed.

Under conditions of 80–85 °C and 38–40 atm., the relative peak area of ethyl acetate was 7.82 %, while that of 1,1-diethoxyethane was 16.72 %. At 100 °C and 30 atm., the corresponding values were 5.86 and 21.88 %, respectively. Thus, among the examined samples, the largest peak area corresponding to ethyl acetate was recorded in the experiment at 80–85 °C, whereas the largest peak area corresponding to 1,1-diethoxyethane was recorded at 100 °C. However, because temperature, pressure, and reaction duration varied simultaneously, these changes cannot be explained solely by the effect of temperature.

The formation of 1,1-diethoxyethane may be discussed in terms of the acetalization equilibrium between ethanol and acetaldehyde. Ethyl acetate may be considered in relation to oxidation and subsequent transformations involving ethanol. Nevertheless, the obtained GC–MS results do not directly confirm the formation mechanisms of these compounds. In particular, the available data do not establish whether ethylene contributed carbon atoms to the molecules of the final products.

A major chromatographic peak corresponding to toluene was also recorded in the experiment conducted at 80–85 °C. However, since toluene was not included in the starting reagents, there is insufficient evidence to consider it a reliable product of the investigated reaction system. Similarly, for certain high-molecular-weight components, library matches alone are insufficient, and possible contributions from solvents or contamination associated with the analytical system must be taken into account. Therefore, these components were not automatically included among the main products.

Another important aspect of the obtained data is that the relative distribution of oxygen-containing components differed under various experimental conditions. This observation indicates that several chemical transformations may occur in the reaction medium. However, the relative chromatographic peak areas of individual components do not allow quantitative conclusions to be drawn regarding the overall conversion, selectivity, or yield of the desired products. These parameters will be evaluated in subsequent studies together with the mass-spectral characteristics of the products.

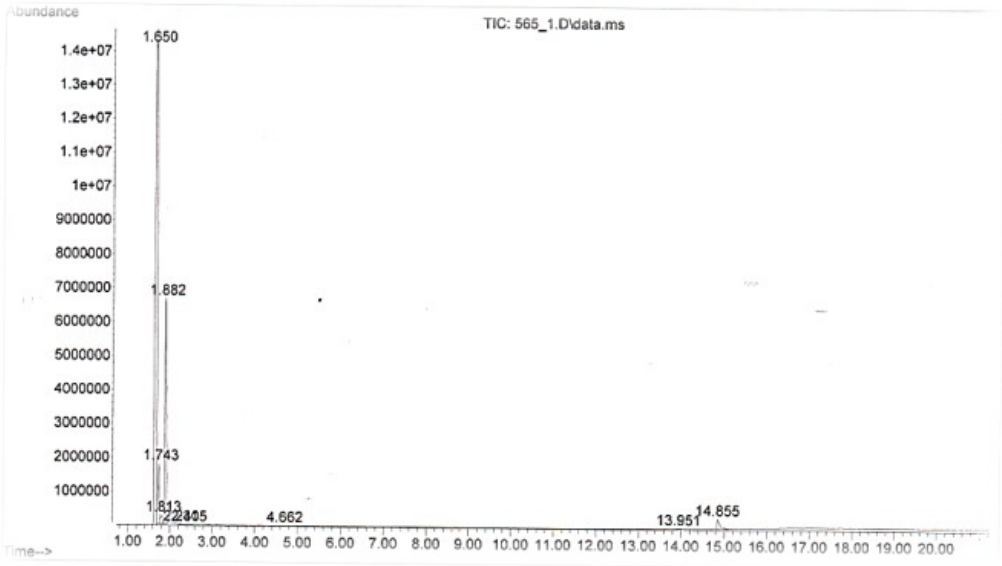

Figure 1. GC–MS chromatograms of mixtures obtained in the ethylene–ethanol system: a — 60 °C

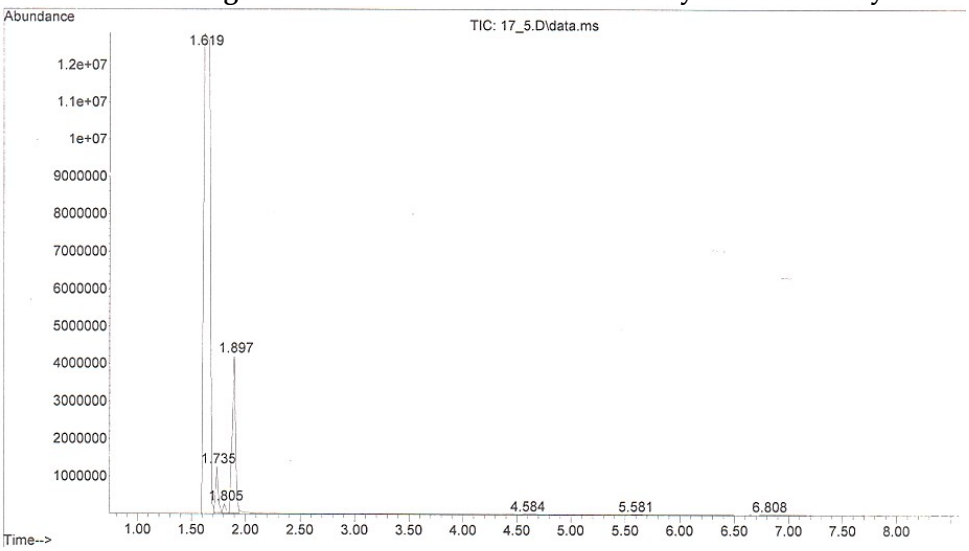

Figure 2. GC–MS chromatograms of mixtures obtained in the ethylene–ethanol system: b — 100 °C.

3.1. Mass-Spectral Analysis of Cyclic Oxygen-Containing Compounds

During the investigation of product mixtures obtained in the ethylene–ethanol system, the mass-spectral characteristics of oxygen-containing compounds with cyclic structures were analyzed separately. According to the preliminary identification data, spectra corresponding to cyclohexanol and methylphenol were recorded. These compounds differ in their molecular structures: cyclohexanol is a saturated alicyclic alcohol, whereas methylphenol is an aromatic compound containing a hydroxyl group. Therefore, it is important to examine their fragmentation characteristics separately.

In the mass spectrum of cyclohexanol ($C_6H_{12}O$), the ion with the highest intensity was observed at m/z 57. In addition, fragments at m/z 82, 67, and 44 were recorded. The signal at m/z 100, corresponding to the molecular ion, exhibited relatively low intensity. In particular, the m/z 82 fragment may be associated with the elimination of water from the molecular ion:

$$C_6H_{12}O^{+\cdot} \rightarrow C_6H_{10}^{+\cdot} + H_2O$$

This fragmentation may be characteristic of cyclic compounds containing a hydroxyl group. The presence of fragments at m/z 57 and 67 may be associated with further fragmentation processes of the carbon skeleton. However, the presence of these fragments alone does not conclusively confirm the structure of cyclohexanol; their relative intensities and agreement with the library spectrum must also be evaluated.

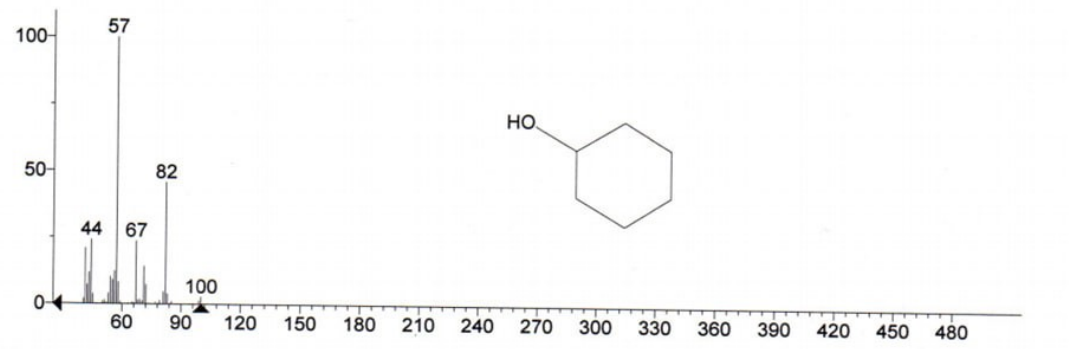

Figure 3. Mass spectrum corresponding to cyclohexanol and its main fragment ions.

In the mass spectrum of methylphenol (C_7H_8O), the molecular ion at m/z 108 exhibited the highest intensity. In addition, fragment ions at m/z 79, 90, 63, and 51 were observed. The relatively high intensity of the molecular ion indicates the stability of the aromatic ring-containing structure under electron ionization conditions. The ions at m/z 79 and 51 may be associated with fragmentation of the aromatic carbon skeleton. The predominance of the molecular ion and the presence of low-mass fragments provide a basis for discussing the library identification corresponding to methylphenol.

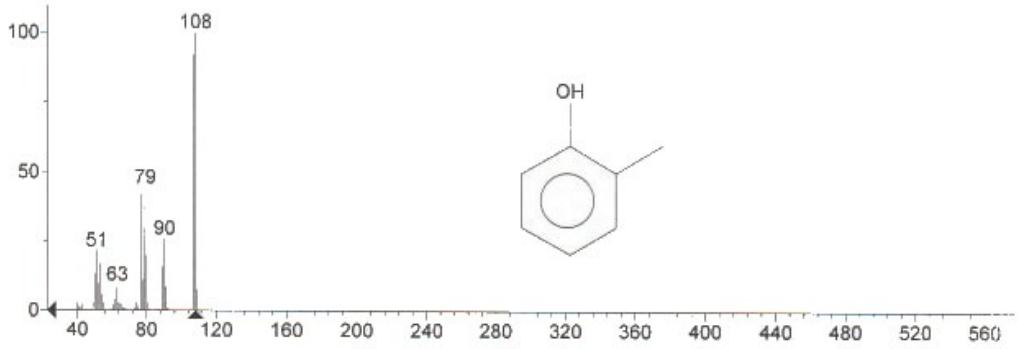

Figure 4. Mass spectrum corresponding to methylphenol and its main fragment ions.

A comparison of the mass spectra of cyclohexanol and methylphenol reveals significant differences in their fragmentation characteristics. In the cyclohexanol spectrum, the m/z 57 fragment is predominant, while the molecular ion exhibits low intensity. In contrast, the molecular ion at m/z 108 forms the main peak in the methylphenol spectrum. This difference is consistent with the structural characteristics of an alicyclic alcohol and an aromatic hydroxyl-containing compound.

At the same time, the presented mass spectra do not independently confirm that these compounds were formed specifically as a result of the ethylene–ethanol reaction. For this purpose, the spectra must be linked to specific peaks in the experimental chromatograms, and their retention times must be compared with library data. Therefore, at the present stage, cyclohexanol and methylphenol were evaluated as possible components. Their observation provides a scientific basis for further investigation of the composition of cyclic oxygen-containing organic compounds.

3.2. Effect of Reaction Conditions on Product Composition

In the reactions of ethylene in an ethanol medium in the presence of hydrogen peroxide and acetone, variations in temperature, pressure, and reaction duration resulted in noticeable differences in the composition of the product mixtures. GC–MS analysis revealed peaks corresponding to oxygen-containing compounds such as ethyl acetate and 1,1-diethoxyethane, and their relative percentages were found to vary depending on the experimental conditions. This indicates that the composition of oxygen-containing organic components in the reaction system is not constant.

At 60 °C and 18–24 atm, the relative chromatographic percentage of ethyl acetate was 3.05 %, whereas at 80–85 °C and 38–40 atm, it increased to 7.82 %. At 100 °C and 30 atm, it was 5.86 %. Similarly, the corresponding values for 1,1-diethoxyethane were 13.94 % at 60 °C and 16.72 % at 80–85 °C. These results indicate a redistribution of the product composition under conditions where temperature and pressure varied simultaneously.

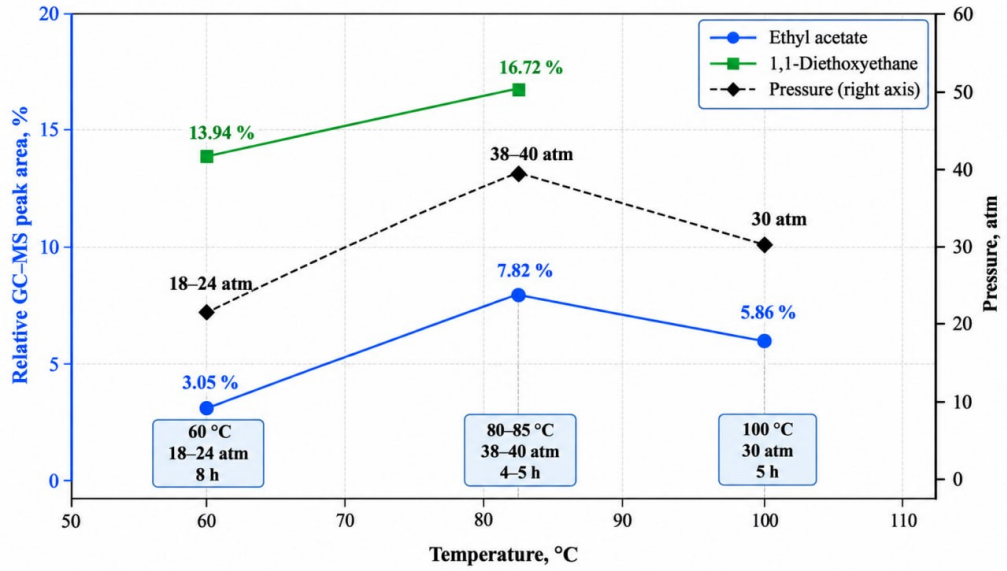

Figure 5. Comparison of the relative GC–MS peak areas corresponding to ethyl acetate and 1,1-diethoxyethane in the ethylene–ethanol system under different experimental conditions.

The observed differences indicate the possible existence of several competing pathways for the formation and subsequent transformation of oxygen-containing components in the ethanol medium. The oxidizing properties of hydrogen peroxide, the influence of acetone on the composition of the reaction medium, and the contact of ethylene with the liquid phase under pressure are important factors characterizing this system. In particular, the experimental conditions at 80–85 °C, where the highest relative peak area corresponding to ethyl acetate was recorded, clearly illustrate differences in component distribution.

The detection of mass-spectral features corresponding to cyclohexanol and methylphenol represents an additional result demonstrating the compositional diversity of the obtained mixtures. The fragmentation characteristics of these compounds were analyzed in Section 3.1. Thus, the GC–MS results indicate that the composition of oxygen-containing organic components in the ethylene–ethanol system varies depending on the experimental conditions. Further experiments in which temperature, pressure, and reaction duration are varied independently are required to determine their effects.

4.Conclusion

The reactions of ethylene in an ethanol medium in the presence of hydrogen peroxide and acetone were investigated at temperatures of 60–100 °C and pressures of 18–40 atm. GC–MS analysis of the resulting product mixtures revealed chromatographic peaks corresponding to ethyl acetate, 1,1-diethoxyethane, and other organic components.

The relative chromatographic percentage of ethyl acetate was 3.05 % at 60 °C, 7.82 % at 80–85 °C, and 5.86 % at 100 °C. The relative peak area of 1,1-diethoxyethane increased from 13.94 % at 60 °C to 16.72 % at 80–85 °C. These results demonstrate that the composition of the mixture changes under different temperature, pressure, and reaction-duration conditions.

Mass-spectral analysis revealed fragment ions corresponding to cyclohexanol and methylphenol. These features provided a basis for suggesting the possible presence of cyclic oxygen-containing compounds and indicated the need to confirm their structures using additional analytical methods.

Overall, the study made it possible to evaluate the formation and compositional changes of oxygen-containing organic components in the ethylene–ethanol system. The obtained data provide a scientific basis for further investigations aimed at a more detailed examination of the effects of reaction conditions on product composition and the isolation of target compounds.

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