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Alkylation of benzene with ethylene in the presence of dimethyldichlorosilane



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1. Introduction

Ethylbenzene (ETB) is a product that is manufactured in excess of several million tons per year. It is used for the production of styrene, its polymers and copolymers, as well as chlorine- and oxygen-containing compounds, and other products [1]. Scientists worldwide have carried out research aimed at the improvement of the production process of ETB through the development of new catalysts and technologies for the alkylation of benzene with ethylene.

The industrial alkylation process of benzene with ethylene, outlined in 1877 by the studies of Friedel, Crafts, and Gustavson, is conducted on polyalkylbenzene in the presence of an aluminum chloride complex.

Approximately 50% of ethylbenzene is produced in the presence of the $Al_2Cl_6 \cdot nArR$ complex. This technology has been implemented and described in articles and monographs by several research groups [1–5].

An important direction of the work of both research groups and educational institutions is the development of effective aluminosilicate zeolites as catalysts for benzene alkylation [6,7].

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ABSTRACT

The kinetics of the alkylation of benzene with ethylene in the presence of dimethyldichlorosilane (DMDCS) are studied and a kinetic equation for this homogeneous irreversible reaction of the second order is created. The circulation of the DMDCS catalyst does not reduce its initial activity in relation to the formation of ethylbenzene and diethylbenzenes. The presence of moisture in the initial $C_{6}H_{6} + C_{2}H_{4} + DMDCS$ mixture reduces the catalyst activity. The dehydration of the starting mixture by removal of moisture from benzene was carried out using an azeotropic distillation. A reaction mechanism for the benzene alkylation with ethylene in the presence of DMDCS is formulated based on the generalized quantum-chemical principle and the theory of groups. The participation of DMDCS in the process of hydrocarbon conversion is confirmed experimentally and theoretically for the first time.

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The number of scientific publications reflects the great deal of research work that has been performed on the alkylation of benzene with ethylene in the presence of homogeneous and heterogeneous catalytic systems [8–22].

The investigation of the alkylation of benzene with ethylene over the faujasite zeolite by the ONIOM method has been described [8]. Beta, MCM-22, USY-1, and USY-2 zeolites have been shown to efficiently activate the C_6H_6 and C_2H_4 molecules for the alkylation of benzene with ethylene in the liquid phase, under pressure and at low temperatures [9]. It has been established that the zeolite activity increases in the order MCM-22 > Beta > USY-1 > USY-2 [18].

In another study, the usage of tablets of clay mixed with aluminum oxide as active catalyst has been described [10].

It has also been established that the reasonable processing of the zeolites MCM-49 and MCM-22 in a 0.025 N sodium hydroxide solution increases the selectivity of the catalyst to ETB up to 97% at P = 3.5 MPa and T = 493 K in the liquid phase [11].

In another reports, the authors postulated that the weak and strong catalytic centers of the MCM-56 zeolite might participate in the catalytic alkylation process [12,13].

The zeolite β exhibits an enhanced catalytic activity [14]. The zeolite MCM-49 possesses a high selectivity, and a correlation has been found between the activity and the content of the Brønsted centers on the zeolite surface and in its lattice [15].

The oxidative alkylation of benzene with ethylene is effective over the ZSM-5 zeolite. [16]. The ETB selectivity in the liquid phase alkylation of benzene with ethylene over the H-TMP-16 zeolite at 200–260 °C reaches 99% [17,18].

An interesting study on the alkylation of benzene with ethylene in the presence of MCM-49 zeolites was also carried out [19]. The mesoporous zeolites are more active (2–10 wt%) in the alkylation of benzene with ethylene in the liquid phase and more selective towards ETB (90–97%), compared to conventional zeolites [20–22,16].

A catalyst based on MCM-22 was used in technology, and named as $EBMax^{TM}$ by Mobil–Raytheon. In this application, the alkylation is performed in the liquid phase. The first industrial application was realized in 1997 [23,24].

In different studies [18–22,16], the mechanism of the alkylation of benzene with ethylene was explained by the presence of {AlO₄-·SiO₄} tetrahedral ensembles in the lattice of zeolites [25–27]. The reaction over the aluminosilicate catalyst surface occurs at the centers of the {AlO₄·SiO₄} tetrahedral ensembles [28–31]. The ensembles of {AlO₆·SiO₄} are catalytically inactive. The basic understanding of the catalysis over zeolites is presented in the theory of catalysis by polyhedra [29–33].

The objective of this work is to develop a new catalyst that is non-toxic, completely soluble in liquid aromatic hydrocarbons, easily separated from the alkylation products during its circulation in the system, and capable of forming environmentally friendly products of hydrolysis.

2. Experimental methods

Experiments involving the alkylation of benzene with ethylene were carried out in an autoclave at elevated pressure (up to 10 atm) and temperatures up to 573 K. The ethylene used in the experiments was of 98.88 wt% purity, while benzene was of chemical purity grade. DMDCS was used as catalyst.

Pre-estimated amounts of benzene and DMDCS were loaded into the autoclave, and ethylene was then injected under pressure.

Benzene was purified by shaking with concentrated H_2SO_4 to remove thiophene, then washed with distilled water, and dried in a desiccator over concentrated H_2SO_4 .

The reaction mixture was analyzed chromatographically. The mixture of benzene and DMDCS was distilled from the reaction mixture on a distillation column to be reused in further alkylation experiments.

3. Results and discussion

3.1. Effect of the DMDCS concentration on the yield of the alkylation products

The study of the alkylation of benzene with ethylene was carried out in an autoclave by varying the DMDCS concentration (10, 20, and 24 wt%) in the reaction mixture and according to the following experimental parameters: T = 513 K, $\gamma = \frac{n_{C_6H_6}}{n_{C_2H_4}} = 3:1$, contact time τ from 0.5 to 5 h, and initial pressure of 10 atm. Ethylene was fed into the autoclave from a cylinder where it was enclosed under a pressure of 50 atm. The results of these experiments are presented in Table 1.

The composition of the products in the reaction mixture was determined chromatographically. Hexene was formed as a result of the ethylene polymerization reaction (trimerization).

According to Table 1, an increase in the yield of ethyl benzene occurs with increasing DMDCS concentrations in the reaction mixture under the initial pressure of 10 atm and temperature of 513 K. The highest yield of ethyl benzene of 28.78 wt% at $\gamma = \frac{n_{c_0H_6}}{n_{c_2H_4}} = 3 : 1$ was obtained at a concentration of DMDCS of 24 wt% and $\tau = 5$ h.

These data are comparable with those obtained by using the aluminum chloride catalytic complex from the industrial alkylation installations.

The advantages of the alkylation process of benzene with ethylene in the presence of DMDCS are:

- complete DMDCS solubilization in aromatic hydrocarbons with the formation of a true thermodynamically stable solution;
- the alkylation takes place in a homogeneous mixture;
- the catalyst is non-toxic and the products of its hydrolysis are environmentally friendly;
- the boiling points of benzene and DMDCS are very close, thus these components can be distilled together out of the reaction mixture for their subsequent circulation through the alkylation unit;
- DMDCS is stable in the reaction mixture in the absence of moisture, and its high activity and selectivity remain unchanged.

In view of this, the DMDCS catalyst favorably differs from the aluminum chloride complex used with polyalkylbenzene.

3.2. Calculation of the equilibrium output

The process of benzene alkylation with ethylene generally occurs at temperatures up to 573 K and atmospheric pressure, and with a molar ratio of benzene to ethylene equal to 3:1. The experiments described in this study were carried out at temperatures ranging from 353 to 573 K, and the thermodynamic parameters were calculated for this range. The standard Gibbs free energy change was obtained according to the equation:

$$\Delta_r G_T^\circ = \Delta_r H_T^\circ - T \cdot \Delta_r S_T^\circ,$$

where $\Delta_r G_T^\circ$ is the standard Gibbs free energy change for the benzene alkylation reaction with ethylene, $\Delta_r H_T^\circ$ is the enthalpy of the reaction, and $\Delta_r S_T^\circ$ is the entropy change of this reaction. These thermodynamic characteristics of the reaction were calculated using the data from the standard heat of formation of benzene, ETB, and ethylene and their standard entropies [34]. The resulting equation is:

$$\Delta G_{T}^{\circ} = -103818 + 142.687 \cdot T$$

in Joules.

The following values of the Gibbs free energy change were obtained:

 $\begin{array}{l} T=353 \ \text{K}, \ \Delta G_{353}^\circ=-53449 \ \text{J/mol}; \\ T=453 \ \text{K}, \ \Delta G_{453}^\circ=-39180 \ \text{J/mol}; \\ T=573 \ \text{K}, \ \Delta G_{573}^\circ=-22058 \ \text{J/mol}. \end{array}$

The calculated equilibrium constants were obtained according

$$K_P = e^{\frac{-\Delta G_T^\circ}{RT}}.$$

to the equation:

The numerical values of the equilibrium constants at T = 353, 453, and 573 K were equal to: $K_{P,353} = 1.23 \cdot 10^8$, $K_{P,453} = 32,960$, and $K_{P,573} = 102.53$.

Therefore, the equilibrium yield of ethylbenzene is 0.999 mol fraction at these temperatures. Consequently, the thermodynamic conditions do not limit the kinetics of the alkylation of benzene with ethylene, and the kinetics of the process reflect the occurring of a kinetically irreversible reaction.

3.3. Kinetics of the alkylation process

The kinetics of the benzene alkylation with ethylene in the presence of DMDCS at the initial pressure of 10 atm, T = 513 K, and molar ratio of benzene to ethylene of 3:1 were studied at

Table 1
Results and conditions for the benzene alkylation with ethylene in the presence of DMDCS as catalyst at $T = 513$ K.

Time (τ), h	DMDCS concentration, wt%	DMDCS concentration, wt% Pressure (P), atm		Product yield	, wt% (± 0.01)		
		Initial	Final	Hexene	C ₆ H ₆	$C_6H_5C_2H_5$	o-DEB
2.0	4	10	9.5	0.32	96.16	3.52	-
3.0	4		8.9	0.59	92.99	6.42	-
5.0	4		7.4	0.98	84.42	14.60	-
0.5	10		9.0	0.52	93.85	5.63	-
3.0	10		8.4	0.79	87.46	11.75	-
5.0	10		6.8	1.34	82.69	15.84	0.13
0.5	20		9.5	0.20	95.77	3.97	0.06
1.0	20		7.5	0.43	93.80	5.68	0.09
2.0	20		7.3	0.46	92.26	7.18	0.10
3.0	20		5.2	1.38	74.84	23.57	0.21

DMDCS concentrations in the mixture of 5, 10, and 20 wt%. The results of these experiments are given in Table 2.

From the data in Table 2, an increase of the product content in the reaction mixture with time and upon increasing DMDCS catalyst concentrations can be observed. When the DMDCS content in the mixture was 20 wt%, the yield of ethylbenzene reached 23.57 wt%, which is close to the yield of ethylbenzene obtained in the presence of the Al₂Cl₆.*n*ArR complex as catalyst.

The kinetics of the process were reflected in the change in the content of the alkylation products in the reaction mixture with increasing τ , C_{DMDS} , γ , and T.

3.4. Role of DMDCS as promoter in the benzene alkylation reaction

In order to increase the ETB yield, the kinetics of the alkylation of benzene with ethylene at T = 553 K in the presence of 2 wt.% of C₂H₅Cl as stoichiometric promoter in a C₆H₆/C₂H₄ = 3:1 mixture and C_{DMDCS} = 10 wt% were studied. The results of the experiments are presented in Table 2.

From the data in Table 2, it can be concluded that under the chosen experimental conditions, in the presence of a promoter for the benzene alkylation with ethylene, an industrial output level of ETB and DEB up to 30 and 8.02 wt%, respectively, can be achieved.

As indicated above, the DMDCS catalyst has several advantages compared to the Al_2Cl_6 .*n*ArR complex widely used in the industry.

3.5. Distillation of the reaction mixture

The distillation of the mixtures of DMDCS with the reaction components was conducted with the aim of plotting the boiling and condensation temperatures in a diagram and determining the possibility for the joint discharge of benzene with DMDS from the reaction mixture.

The distillation of the liquid hydrocarbon compounds from the mixtures of DMDCS + benzene and DMDCS + ETB was carried out on a standard apparatus for sampling of the liquid and vapor fractions.

The sampling of the DMDCS + benzene and DMDCS + ETB mixtures during the distillation was carried out through 5° and 10° , respectively. The results of the distillation of the DMDCS + benzene and DMDCS + ETB mixtures are shown in Figs. 1 and 2.

From Fig. 1, it can be seen that the curve of the vapor condensation (curve 1) is close to the evaporation curve (curve 2). Therefore, C_6H_6 and DMDCS are difficult to separate, and can be evaporated together from the liquid phase and circulate through the reactor unit. In Fig. 2, the curves of the DMDCS and ETB mixture distillation are located at a considerable distance from each other. Thus, it is possible to completely separate ETB from the DMDCS and benzene mixture.

3.6. Effect of the DMDCS concentration on the yield of the alkylation products

The effect of the DMDCS concentration on the alkylation of benzene with ethylene was studied at T = 513 K, γ = 3:1, C_{DMDCS} = 5, 10, 20, and 24 wt%.

The reaction autoclave was placed on an electromachine with a frequency of 1 swing every 2 s. The heating of the reaction mixture was carried out with an electric furnace. At the end of the experiment, the autoclave was cooled to room temperature. The unreacted ethylene was released into the gas meter. The reaction mixture was analyzed by chromatography using a Chromos GH-1000 chromatograph. The results of these experiments are presented in Table 3.

On the basis of the data in Table 3, upon increasing the DMDCS concentration in the initial reaction mixture from 5 to 24 wt%, the ETB yield rose for each feedstock and catalyst contact in the autoclave, while o-DEB appeared only when $C_{DMDCS} = 10$ wt% and $\tau = 3$ h.

The maximum yield of ethylbenzene was obtained when the contact time of the reaction mixture with the catalyst (τ) was 5 h and the DMDCS concentration was 10–24 wt%. The output of ETB was 23.36–28.78 wt%, while the DEB yield was 0.64–1.82 wt%.

3.7. Effect of the temperature on the yield of the alkylation products

According to the van't Hoff rule, the velocity of chemical reactions undergoes a twofold increase or more for each temperature rise of 10 °C. Therefore, the experiments for the alkylation of benzene with ethylene were conducted in the temperature range

Ta	ble	2

Results and conditions for the benzene alkylation with ethylene in the presence of 2 wt% of C_2H_5Cl .

Time, h	Pressure (P), atm		Product yield, wt	Product yield, wt% (± 0.01)			
	Initial	Final	Hexene	Benzene	ETB	DEB	
0.5	10	7.6	0.11	88.11	11.3	0.48	
3.0		4.5	0.46	72.84	23.3	3.40	
5.0		3.0	1.12	60.06	30.8	8.02	



Fig. 1. Distillation diagram of a benzene and DMDCS mixture under atmospheric pressure. 1: liquid evaporation curve, 2: vapor condensation curve.



Fig. 2. Diagram of the distillation of the mixture of ETB with DMDCS. 1: liquid phase, 2: vapor.

Table 3								
Composition	of the	reaction	mixture;	T =	513	К, 1	γ =	3:1

T = 513–573 K at C_{DMDCS} = 20 and 50 wt%, τ = 3 h, and γ = 3:1, and the reaction mixture was further analyzed by using a gas chromatograph. The results of these experiments are given in Table 4.

It can be noted from the data in Table 4 that upon increases of the temperature, the ETB yield reached a maximum at T = 533 K. This may be associated with the higher content of dimers of ethylene and DEB in the reaction mixture. As shown above in this temperature range, there are no thermodynamic restrictions for the reaction influencing the yield of ETB.

3.8. Effect of moisture on the DMDCS activity

In the presence of moisture in the reaction mixture, the hydrolysis of DMDCS may occur according to the scheme $(CH_3)_2SiCl_2 + H_2O ===> (CH_3)_2SiClOH + HCl$, leading to a decrease of the catalyst activity. To prove this assumption, experiments were conducted by adding 0.1 and 0.3 cm³ of water in the autoclave (see Table 5).

From the data in Table 5, it follows that with the addition of 0.1 and 0.3 cm^3 of water to the 50 cm³ of the initial reaction mixture, the output of ETB and DEB decreases 1.79 and 2.86 times, respectively.

These data confirm that the moisture in the reaction mixture hydrolyzes DMDCS. Hence, it is necessary to dry the initial reaction mixture containing benzene, ethylene, and DMDCS up to 10–5 ppm of moisture.

3.9. Kinetic equations

Kinetic studies allow building models for the management of technological alkylation processes. This section is devoted to the kinetics of the alkylation process and the creation of mathematical descriptions.

The study of the reaction kinetics of the benzene alkylation with ethylene was conducted at temperatures ranging from 433 to 533 K, $P_{initial} = 10$ atm, $\tau = 3:1$, $C_{DMDCS} = 10$ wt%, and reaction times from 1 to 3 h. The results of these experiments are presented in Table 6.

From Table 6, it can be seen that a regular increase of the dimers, ETB content, and the sum of the DEB products occurs with the rising of T and τ . For these experimental patterns, a kinetic equation linking the conversion with the timing of the experiments and the concentration of DMDCS in the mixture was obtained as follows:

$$\frac{1}{1-x} - 1 = k \cdot V \cdot \frac{\gamma}{1+\gamma} \cdot P_0 \cdot \tau, \tag{1}$$

where *x* is the feedstock conversion, γ is the C₆H₆/C₂H₄ ratio, P₀ is the initial pressure of the reaction mixture (atm), τ is the reaction

Time (τ), h	C _{DMDCS} , wt%	Pressure (P), atm		Alkylate comp	osition, wt% (±0.01)		
		Initial	Final	Hexene	Benzene	ETB	o-DEB
2	4	10	9.5	0.32	96.14	3.54	-
2	10		9.1	0.36	93.99	5.65	-
2	20		7.5	0.42	92.40	7.18	-
2	24		6.2	0.53	91.15	8.32	-
3	4		8.9	0.51	93.07	6.42	-
3	10		6.8	0.62	87.42	11.75	0.21
3	20		5.2	0.79	80.48	18.31	0.42
3	24		4.7	0.88	78.55	20.01	0.56
5	4		6.8	0.78	83.10	15.89	0.23
5	10		5.0	0.98	75.02	23.36	0.64
5	20		4.4	1.53	73.22	23.80	1.45
5	24		3.81	1.68	67.72	28.78	1.82

Table 4

Effect of the temperature on the yield of ethylbenzene.

Т, К	P, atm		Product yield, wt	Product yield, wt% (±0.01)			
_	Initial	Final	Hexene	Benzene	ETB	DEB	
513	10	7.6	1.05	82.70	15.98	0.27	
533		7.0	1.24	76.85	21.18	0.73	
553		7.5	1.53	82.12	15.33	1.02	
573		7.8	2.86	81.80	14.16	1.18	

Table 5

Results of the benzene alkylation with ethylene at T = 533 K, τ = 3 h, γ = 3:1, C_{DMDCS} = 20 wt% in the presence of water.

P, atm		H_2O , cm^3	Alkylate composition, wt% (±0.01)			
Initial	Final		Ethylene dimer	Benzene	ETB	DEB
10	7.5 8.6	0.1 0.3	0.36 0.15	85.41 91.51	14.6 8.12	0.63 0.22

Table C			
rable b			

Kinetics of the alkylation of benzene with ethylene in an autoclave: $P_{initial} = 10 \text{ atm}$, $C_{DMDCS} = 10 \text{ wt\%}$, $\gamma = 3:1$.

Time (τ), h	n T, K Product yield, wt% (±0.01)				Final pressure, atm		
		C_4H_8	C ₆ H ₆	ETB	DEB		
					0-	<i>m</i> -+ <i>p</i> -	
1	433	-	98.28	1.72	-	-	9.97
2	433	-	97.19	2.81	-	-	9.72
3	433	-	95.12	4.88	-	-	9.51
1	473	-	97.80	2.11	0.03	0.06	9.54
2	473	-	93.77	5.92	0.11	0.2	9.14
3	473	0.10	90.78	8.66	0.23	0.33	9.06
1	513	0.12	95.61	4.20	0.07	0.12	9.56
2	513	0.18	90.13	9.40	0.19	0.28	9.06
3	513	0.24	86.94	11.80	0.73	0.53	8.72
1	533	0.16	93.77	7.50	0.16	0.22	9.25
2	533	0.22	90.78	12.50	0.28	0.62	86.99
3	533	0.34	95.61	17.80	0.65	0.71	80.84

time (h), *V* is the volume (dm³), and *k* is the reaction rate constant (dm⁻³·atm⁻¹·h⁻¹).

The rate reaction constants were calculated based on the data in Table 6 and equation (1); the results are summarized in Table 7 (V = 0.1 dm³; γ = 3; P₀ = 10 atm; τ = 1, 2, 3 h).

According to the data in Table 7, an Arrhenius graph is plotted as shown in Fig. 3. The data from Table 7 were treated using the least square method for finding the coefficients of the linear equation: $\ln k = -(\frac{E_a}{R}) \cdot \frac{1}{T} + \ln A$, where E_a is the activation energy, R = 8.314 J/(mol-K) is the gas constant, and A is the pre-exponential factor.

The activation energy of the benzene alkylation with ethylene and the pre-exponential factor in the Arrhenius equation were calculated from the following expression:

 $\ln k = -\frac{3006.9}{T} + 3.092$, where $E_a = 25,709$ J/mol, A = 22.03.

The numerical value of the activation energy indicates a higher catalytic activity of DMDCS in the benzene alkylation reaction with ethylene.

Table 7	
Calculated values of the reaction	rate constant k and data for the Arrhenius plot.

Т, К	k, dm ⁻³ ·atm ⁻¹ ·h ⁻¹	$1/T, K^{-1}$	lnk
433	0.023	0.00231	-3.7723
473	0.035	0.00211	-3.3524
513	0.052	0.00195	-2.9565
533	0.095	0.00188	-2.3539



Fig. 3. Arrhenius plot for the benzene alkylation reaction with ethylene.

3.10. Catalyst circulation

The process of the alkylation of benzene with ethylene was carried out at T = 533 K, P_{Initial} = 10 atm, γ = 3:1, and τ = 3 h. The results of these experiments are shown in Table 8.

Only the data of 3 out of 9 experiments are given in Table 8. The use of any benzene + DMDCS mixture, selected from the previous experiments, did not change the yield of the reaction products. The activity of DMDCS did not change in the absence of moisture during the 9 experiments, confirming the perspective of the DMDCS application in the technology of the benzene alkylation with ethylene.

80

Table 8

DMDCS circulation in the benzene alkylation with ethylene, $\tau = 3$ h.

Number of experiments	Final pressure, atm	Yield, wt% (±0.01)				
		C ₄ H ₈	C ₆ H ₆	$C_6H_5C_2H_5$	DEB	
					0-	m-
1	8.68	0.28	86.32	12.13	0.66	0.61
4	8.32	0.42	86.29	11.88	0.69	0.72
9	8.42	0.48	86.02	12.16	0.66	0.68



Fig. 4. Scheme of the ethylbenzene synthesis in the presence of a catalyst $K = SiR_mCl_p$, where $R = CH_3$, m = 2, and p = 2.

The circulation of the catalyst in the reaction flow system is an important economic, technological, and environmental factor. It determines the catalyst minimal loss, and it is necessary to create the conditions for the alkylation process that avoid the presence of moisture in the raw material and catalyst, enabling the operation of the DMDCS catalyst for a long time with its minimal addition into the reactor.

3.11. Alkylation mechanism

In a previous study, it was found that the C_2H_4 molecules deriving from the mixture of C_2H_4 and C_6H_6 are initially adsorbed over zeolites and undergo excitation ($C_2H_4 \rightarrow *C_2H_{4ads}$) [17]. Subsequently, they are joined by the benzene molecules and the catalytic reaction proceeds with the formation of ETB and other compounds according to a carbocationic mechanism.

Taking into account this information, and in accordance with the theory of catalysis by polyhedra [30–33,35] and the generalized quantum-chemical principle [35], it is possible to provide more precise quantum-chemical calculations of the cyclically occurring process of benzene alkylation with ethylene in the presence of DMDCS.

According to the theory of catalysis by polyhedra [29–33,36], "the catalytic center in solid catalysts (in solutions) is a polyhedron of a certain composition, structure, state, and symmetry". The active catalytic center in zeolites and aluminosilicates is the ensemble of AIO_4 ·SiO_4}-tetrahedra. Based on this theory, it is approved the only cycle of a catalytic process which is formulated reasonably as the only mechanism. The same process will occur with the SiR_mCl_p tetrahedra.

The generalized quantum-chemical principle states: "a chemical catalytic reaction can take place at all elementary stages, while simultaneously fulfilling the requirements imposed on the reacting system substances by the Hund's rule, the Pauli exclusion principle, the matching of the energies, the phase signs of the orbitals, and the Woodward–Hoffmann orbital symmetry: the violation of any of these requirements imposes a prohibition on the occurring of the elementary stages of the reaction or increases the probability of its breakage [36]. In accordance with this statement, the mechanism of the benzene alkylation with ethylene can be represented by the cyclic scheme in Fig. 4.

This scheme can explain the elementary steps of the alkylation, which include:

- diffusion of the molecules of benzene to the K (SiR_mCl_p) catalyst molecules;
- interaction of the π^0 -LUMO of the C₆H₆ molecules with the 3d⁰-AO of the Si⁴⁺ ions in the tetrahedron [SiR_mCl_p] and formation of the intermolecular complex [K^{δ -}C₆H^{δ +}]. According to the group theory, the product of the irreducible representations in this situation is equal to the fully symmetrical representation $G_\beta \cdot G_\beta = G_\alpha$; thus, this interaction is allowed by symmetry;

Table 9 Calculated MP2/aug-cc-pVDZ energies of benzene, ethylene, DMDCS, and ETB.

Compound	Energy, MJ/mol	Excitation energy,	
	Basic singlet state	Lowest excited triplet state	kJ/mol
Ethylene Benzene DMDCS ETB	-205.7 -607.9 -3381.8 -813.7	-205.4 -607.5 -	288.1 443.9 -

Table 10

Calculated MP2/aug-cc-pVDZ energies of benzene, ethylene, DMDCS, and ETB intermolecular complexes and interaction energies (Eint) of the molecules in these complexes.

Intermolecular complex	E, MJ/mol	E _{int} , kJ/mol	E _{int} ^a , kJ/mol
DMDCS + C_2H_4	- 3587.4	-7.5	-295.6
DMDCS + C_6H_6 DMDCS + C_6H_6 + C_2H_4	- 3989.7 - 4195.4	-14.3 -28.2	-458.2 -316.3
DMDCS + ETB	- 4195.5	-6.3	_

Interaction energy between the molecules within the complex, when the C₂H₄ molecules (or C_6H_6 in DMDCS + C_6H_6) are in the lowest triplet state.

- diffusion of the ethylene molecules in the electromagnetic field of the [SiR_mCl_n]-tetrahedron, excitation, and formation of the intermolecular complex $[K^{\delta-}C_6H_6^{\delta+}] \cdot C_2H_4^*$.
- redistribution of the electrons and bonds in the complex $K^{\delta-1}[C_2 H_4:C_6H_6]*^{\delta^+}$ with formation of an intermolecular complex of K with the ETB molecules, i.e., $K^{\delta} \cdot [C_6H_5 \cdot C_2H_5] *^{\delta+}$;
- emission of the quantum of energy (-hv) from the excited ETB molecules and their transition to the ground state;
- decomposition of the ETB complex with K and diffusion of the molecules in the ground state into the bulk of the reaction mixture. Thus, the group production theory $G_{\pi^2} \cdot G_{\alpha^0} = G_\beta$ gives an incompletely symmetric representation that determines the decomposition of the physically adsorbed ETB. However, the ETB delay in the active center in accordance to the scheme may result in the alkylation of ETB with ethylene.

To justify the above mechanism of the benzene alkylation with ethylene, quantum-chemical calculations of the excitation energy of the molecules of benzene and ethylene in the lowest triplet state were carried out, the equilibrium geometry of the bimolecular complexes of DMDCS with benzene and ethylene in the ground and excited states were determined, and the structure of the benzene + ethylene + DMDCS trimolecular complex was obtained.

The calculations were performed using the second order Moller-Plesset perturbation theory MP2 in the basis set aug-cc-pVDZ.

The results of the energy calculations of the isolated molecules and their complexes are given in Tables 9 and 10.

It is evident from the data in Table 10 that the benzene molecules in their singlet state form a more stable intermolecular complex with DMDCS than ethylene, since their interaction energy in the DMDCS + C_6H_6 complex is -14.3 kJ/mol, while for the DMDCS + C_2H_4 complex this energy is -7.6 kJ/mol. Such energy values indicate that in these complexes the intermolecular interactions are Van der Waals interactions.

The highest calculated interaction energies between the molecules were obtained for complexes that include ethylene or benzene molecules in the lowest triplet state. The excitation energy of C_2H_4 was lower than that of C_6H_6 since the probability of a complex formation with ethylene in the triplet state is the highest. The energy excess in such complexes can be spent on the redistribution of the electron density between the molecules and formation of ETB as benzene alkylation product.

4. Conclusion

Experimental studies on the homogeneous catalytic alkylation of benzene with ethylene in the presence of DMDCS as a new high efficiency catalyst showed the possibility to perform a homogeneous synthesis of ETB under mild conditions. The catalyst properties allow its wide application in industrial processes. To control the operation of this novel technology installation, a kinetic equation was created and a mechanism for the alkylation process based on the theory of catalysis by polyhedra was formulated. Quantumchemical calculations confirmed the stages of the interaction between the reactants and the catalyst.

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