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Dimerization of α-Methylstyrene in the Presence of Mordenite, Aimed at Preparation of Transformer Oils

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Abstract—Dimerization of α-methylstyrene in the presence of natural mordenite and its modified form was studied. The dependence of the yield and composition of the products on the process parameters was found. Conditions were determined for preparing linear dimers with a high selectivity.

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Linear and cyclic dimers of α-methylstyrene are widely used as plasticizers, as polymer and rubber modifiers, and in production of synthetic oils [1–4].

High-purity transformer oils are widely used in the modern oil-filled power systems of electrical equipment, in hydraulic systems of engineering apparatus, and in various composite materials as the base of insulating, cooling, and shock-absorbing fluids and film-forming compounds [5, 6]. Therefore, it is important from both scientific and practical viewpoints to find high-performance synthetic carbon compounds of reproducible composition and quality that can be prepared on the basis of α-methylstyrene dimerization products and meet the existing requirements.

Various homogeneous and heterogeneous acid catalysts are suggested for preparing the dimers: organic and mineral acids, metal oxides, acid clays, and cation-exchange resins of various grades [7–9]. In the synthesis of linear α-methylstyrene dimers, crystalline luminophores were used as catalysts, and a linear dimer was obtained at a total α-methylstyrene conversion of 94% [10]. However, such catalytic systems are unique, and their commercial use is economically unfeasible. Talzi et al. [11] prepared α-methylstyrene dimers using zeolite Y as catalyst. They showed that the synthesis of linear dimers with a high selectivity and good yield can be performed in CH_2Cl_2.

In this study we examined oligomerization of α-methylstyrene in the presence of natural mordenite and its modified form without a solvent. We also examined the possibility of using the dimerization products obtained as the base for transformer oils.

It is known that dimerization of α-methylstyrene **I** yields 2,4-diphenyl-4-methyl-1-pentene (α-isomer) **II**, 2,4-diphenyl-4-methyl-2-pentene (β-isomer) **III**, and 1,1,3-trimethyl-3-phenylindan (crystalline cyclic dimer) **IV**. The first two compounds are linear unsaturated dimers, and the third compound is a cyclic saturated dimer (see the Scheme).

Dimerization of α-methylstyrene **I** was performed in the temperature range 30–140°C in the presence of 5–15 wt % natural mordenite. The effect of various

Scheme.

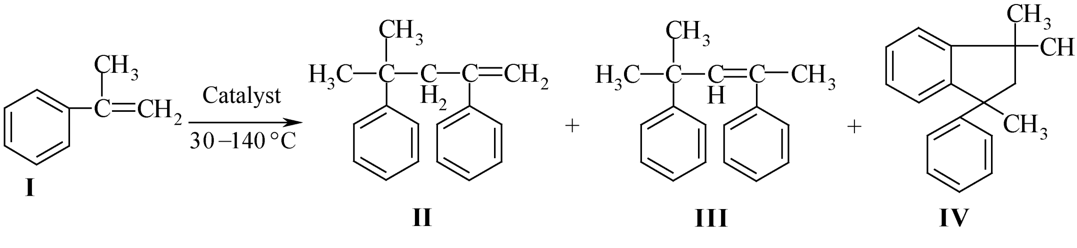

Table 1. Influence of reaction conditions on dimerization of α-methylstyrene **I** in the presence of natural mordenite

T, °C	c_{cat}, wt %	τ, h	Composition, wt %					Conversion	Selectivity
			I	linear		**IV**	trimers	wt %	
				II	**III**				
30	10	2	78.4	18.4	3.2	–	–	21.6	100.0
60	5	1	65.7	30.1	3.7	0.4	0.1	34.3	98.3
	10	1	50.7	43.6	5.0	0.5	0.2	49.3	98.6
	15	1	39.2	50.4	9.2	0.8	0.4	60.8	98.0
	15	2	28.7	56.3	13.4	1.2	0.4	71.3	97.7
80	15	1	30.8	54.5	13.0	1.2	0.5	69.2	97.5
	15	2	32.6	49.1	15.3	1.9	1.1	67.4	95.5
	15	0.5	40.7	48.0	9.0	1.4	0.9	59.3	96.1
100	15	0.5	20.1	59.7	14.8	3.4	2.0	79.9	93.2
	15	1	17.8	60.4	27.2	3.7	3.9	91.3	82.2
120	15	1	9.7	37.4	30.2	18.5	4.2	90.3	74.9
140	15	1	0.9	28.2	34.6	29.4	7.9	99.1	62.3

factors on the conversion and selectivity of dimerization is demonstrated by Table 1.

At a catalyst concentration of 5–10 wt % and a temperature of 30°C, α-methylstyrene transforms slowly: The maximal conversion of α-methylstyrene is as low as 21.6 wt %. However, the selectivity with respect to linear dimers **II** and **III** reaches 100 wt %. With increasing temperature, the reaction rate noticeably increases, and at 100°C the yield of the linear dimers reaches 78.6 wt %, with the content of the cyclic dimer and trimers of 3.7 and 3.9 wt %, respectively. As the reaction temperature is increased over 120°C, the yield of cyclic dimer **IV** increases, reaching 29.4 wt % at 140°C.

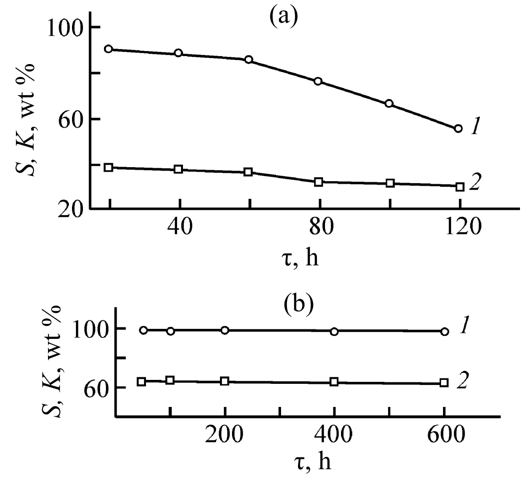

Fig. 1. Dimerization of α-methylstyrene in the presence of (a) initial and (b) modified mordenite as a function of time τ. (*1*) Selectivity *S* with respect to liquid dimers and (*2*) *K*, α-methylstyrene conversion.

In the presence of mordenite as catalyst, α-methylstyrene initially dimerizes to form liquid dimers **II** and **III** as major products. Despite high catalyst selectivity with respect to α-methylstyrene, the conversion in the first 50 h remains virtually unchanged and does not exceed 40% (Fig. 1a). After a certain period (60 h), the yield of liquid dimers **II** and **III** decreases and the content of crystalline cyclic dimer **IV** somewhat increases.

To eliminate these drawbacks and undesirable phenomena, we studied the dimerization of α-methylstyrene in the presence of a natural zeolite, mordenite modified with sulfuric acid in the continuous mode.

Mordenite was preliminarily subjected to hydrothermal treatment by contacting with distilled water at 170–180°C under the required pressure. Then the support was dried at 300°C and treated with sulfuric acid. The results of α-methylstyrene dimerization in the presence of modified mordenite are shown in Fig. 1b.

It can be seen that the results obtained with sulfuric acid treated mordenite as catalyst differ from those obtained with unmodified mordenite. For example, at a constant temperature of 80°C, the conversion of α-methylstyrene is 68.7 wt % irrespective of the reaction time. Experiments performed for 600 h proved that the selectivity with respect to liquid dimers remained essentially unchanged, 97–98 wt %.

The temperature dependence of α-methylstyrene dimerization in the presence of modified mordenite is presented in Table 2.

Table 2 shows that, starting from 80°C, dimerization of α-methylstyrene becomes intense, and at 90°C the yield of dimers **II** and **III** reaches 80 wt %. However, starting from 100°C, the selectivity with respect to liquid dimers starts to decrease, and on reaching 120°C the weight fraction of crystalline dimer **IV** and of trimers dramatically increases. It should be noted that the yields of α-methylstyrene trimers and tetramers on this catalyst at temperatures of up to 90°C do not exceed 2 wt %. This phenomenon confirms the coarsely porous structure of the treated catalyst (mordenite), because α-methylstyrene dimerization in the system is kinetically controlled with no diffusion hindrance.

An increase in the yield of liquid dimer **III**with an increase in the time of contact of α-methylstyrene with the catalyst and in the temperature shows that, in dimerization of α-methylstyrene, α-isomer of linear dimer **II** is formed first, and the β-isomer is formed by its isomerization.

Thus, the developed heterogeneous catalyst can be suggested for an environmentally safe, power-saving, and highly efficient procedure of the synthesis of the linear dimer, 2,4-diphenyl-4-methyl-1(2)-pentene, from α-methylstyrene with a small number of process steps.

The structure of the unsaturated linear dimers prepared was studied by IR, UV, and ^{1}H NMR spectroscopy. In the IR spectrum of 2,4-diphenyl-4-methyl-1(2)-pentene, along with the bands at 3070, 3020, 765, and 705 cm^{-1}, belonging to two phenyl groups, we found absorption bands at 3090 and 855 см$^{-1}$, characteristic of the substituted C=C double bond. The structure of 2,4-diphenyl-4-methyl-1(2)-pentene is well consistent with the ^{1}H NMR spectrum in which we observed the following signals: a multiplet at 7.09 ppm belonging to ten protons of two phenyl rings; a singlet at 6.0 ppm, characteristic of the single proton at the multiple bond (=CH–); a singlet at 1.53 ppm, belonging to three protons of the methyl group at the C=C double bond (CH_3–CH=CH–); and, finally, a singlet at 1.1 ppm, belonging to six protons of the remaining two methyl groups. The ratio of the integral intensities of these signals is 10 : 1 : 3 : 6, suggesting the presence of 20 protons in the molecule of the linear dimer.

Table 2. Parameters of α-methylstyrene dimerization at various temperatures

T, °C	Conversion	Selectivity with respect to liquid dimers **II**, **III**
	wt %	
20	10.0	100.0
40	25.0	99.7
60	48.4	99.2
80	68.6	98.7
90	80.0	97.0
100	87.0	94.0
120	89.7	67.0
140	95.1	57.6

The presence of a conjugated vinylphenyl group in the molecule of the liquid dimer is well confirmed by the UV spectrum of this compound, in which we found a band at $\lambda = 0.251$ nm, disappearing upon hydrogenation of dimers **II** and **III**.

The synthesized α-methylstyrene dimers were analyzed by GLC. As references we used individual dimers synthesized according to [12].

With the aim to decrease the hygroscopicity of liquid dielectrics, improve their gas resistance, and reduce tarring of the base of transformer oils, we examined α-methylstyrene dimerization products (mixture of **II–IV**).

The structural-group compositions of a mixture of α-methylstyrene dimers **II–IV** and of typical commercial oils are given in Table 3. The properties and physicochemical parameters of commercial transformer oils TK, T-750, and GK are described in detail in [13].

Table 3 shows that the mixture of α-methylstyrene dimers is a highly aromatized oil. Therefore, synthetic hydrocarbon oils based on α-methylstyrene dimers **II–IV** are low-viscosity light yellow mobile liquids, resistant to oxidation and nonhygroscopic. These oils are compatible in definite ratios with functional and nonfunctional oligomeric and polymeric substances, solvents, and plasticizers. They

Table 3. Structural-group composition of synthetic hydrocarbons (mixture of **II–IV**) and of GK and T-750 oils

Parameter	Mixture of **II–IV**	GK	T-750
Relative content of carbon atoms, wt %			
in aromatic rings	66.7	1.6	17.0
in naphthene rings	0	40.3	40.0
in paraffin chains	22.4	58.1	43.0
in olefin chains	11.1	0	0

Table 4. Physicochemical and dielectric properties of samples of dimers **II–IV** with different content of **IV**

Parameter	Sample 1	Sample 2	Sample 3
Content of cyclic dimer **IV**, %	2.0	9.8	18.0
Density, g cm^{-3} (at 20°C)	0.9679	0.9681	0.9687
Refractive index	1.5660	1.5620	1.5440
Kinematic viscosity, mm^2 s^{-1}:			
20°C	16.2	20.2	24.1
50°C	5.5	6.3	6.8
Acid number, mg KOH/g	0.007	0.008	0.009
Flash point in closed crucible, °C	164	166	160
Dielectric loss tangent at 90°C, %	1.8	4.60	6.56
Rate of gas absorption, μl min^{-1}	–133.8	–183.3	–200
Breakdown voltage of dried liquid, kV	72	–	–

exhibit high thermodynamic stability and have relatively low vapor pressure (volatility).

As noted above, dimerization of α-methylstyrene yields also a crystalline dimer whose amount can be controlled by using various catalysts and by varying the temperature and time of the reaction. We examined how the concentration of the crystalline dimer affects the physicochemical and dielectric properties of the dimerization products (Table 4).

As seen from Table 4, an increase in the concentration of crystalline dimer **IV** to 18% only weakly affects the physicochemical and dielectric properties of the products.

The set of the examined physicochemical properties and service characteristics of oils is indicative of their high thermodynamic stability in a wide temperature range, which makes them suitable as base components of various formulations, including insulating liquids.

Table 5. Quality parameters of dimers **II–IV**

Characteristic	Dimers **II–IV**	GK
Boiling point, °C	302.0	–
Flash point in closed crucible, °C	164.0	No less than 135
Congealing point, °C	–54.0	Below –45
Glass transition point, °C	–103.0	
Viscosity, mm^2 s^{-1}:		
20°C	16.2	–
50°C	5.5	no more than 9.0
Density, g cm^{-3} (20°C)	0.9679	0.895
Refractive index n_D^{20}	1.5660	–
Temperature, °C, of indicated weight loss, %:		
10	240	
30	278	
50	300	
Heat of formation, kcal kg^{-1}:		
Experimental	–317	
Calculated	–328	
Oxidation resistance (155°C, 50 ml O_2/min):		
(a) 14-h		
test content of volatile acids, mg KOH/g	0.01	no more than 0.04
acid number, mg KOH/g	0.02	no more than 0.10
(b) oxidation time, h, up to indicated acid yield		
0.05 mg of KOH	34.0	22.5
0.25 mg of KOH	86.0	25.0
difference, h	52	2.5

The existing insulating liquids based on transformer oils contain 0.3% Ionol (2,6-di-*tert*-butyl-4-methylphenol) as antioxidant. By analogy, to oils based on α-methylstyrene dimers we also added 0.3% Ionol. The physicochemical parameters of the resulting formulations in comparison with GK and T-750 commercial oils were evaluated by standard methods used in electrical engineering [13]. The results of studying the physicochemical and insulating characteristics of α-methylstyrene dimerization products **II–IV** containing 0.3% Ionol are given in Table 5.

As seen from Table 5, in a high-intensity electric field, α-methylstyrene dimerization product **II–IV** appreciably surpasses commercial transformer oil GK in the stability and therefore is preferable for use in cables, capacitors, and hermetic lead-ins.

Dimers **II–IV** also surpass GK and T-750 oils in gas resistance (Table 6).

Evaluation of the resistance to formation of partial discharges showed that, whereas for commercial transformer oil T-750 the gas evolution coefficient is 84.0 μl J^{-1}, in dimers **II–IV** the partial discharge is absent and no gas evolution is observed (Table 7). It should be noted that gas evolution in liquid dielectrics is inadmissible, and its value characterizes the extent of hazard under the action of electric field.

As already noted, the main requirement to liquids for transformers and capacitors is their high resistance to formation of partial discharges under the action of an electric field.

Monitoring of the oxidation kinetics of oils by the yield of volatile acids shows that, whereas in oxidation of GK and T-750 oils the oxidation occurs in 22.5 and 20.5 h, respectively, with dimers **II–IV** intense oxidation is observed only after the lapse of 180 h, i.e., the dimers exhibit high insulating stability.

High concentration of aromatic rings and the presence of an unsaturated bond predetermine the high stability of dimers **II–IV** to the electric field. The tested product can replace phenylxylylethane presently used for power capacitors.

Thus, synthetic alkenylaromatic oils based on α-methylstyrene dimers are suitable as base components of transformer and capacitor oils, meeting all the IEC requirements.

EXPERIMENTAL

X-ray phase analysis was performed with a DRON-3M diffractometer. The results of X-ray determination of the SiO_2, Al_2O_3, and Fe_2O_3 content were confirmed by atomic-absorption determination of the corresponding metals. Measurements were performed with an AAS-300 spectrometer in air–acetylene and N_2O–acetylene flames. The results were as follows (ppm): SiO_2 78.3, Al_2O_3 78.0, and Fe_2O_3 0.5.

The IR spectra of dimer samples were recorded on a UR-20 spectrophotometer from thin liquid films, and the UV spectra, on a Specord spectrophotometer in quartz cells 0.1 and 1.0 cm thick. The 1H NMR spectra were taken on a Tesla BS-487 spectrometer (80 MHz) at 20°C, with HMDS as internal reference. Liquid products were analyzed with an LKhM-80 chromatograph under the following conditions: flame ionization detector, 300 × 0.3-cm column, stationary phase 7% SE-30 on Chromaton N-AW, carrier gas flow rate 45 cm^3 min^{-1}, vaporizer temperature 315°C, programmed column heating from 90 to 290°C at a rate of 6 deg min^{-1}.

Table 6. Gas resistance of dimers **II–IV** and of GK and T-750 oils in an electric field in a hydrogen medium (IEC* procedure)

Parameter	Dimer **II–IV**	GK	T-750
Gas evolution rate, μl min^{-1}	–	28	–
Gas absorption rate, μl min^{-1}	–133.8	–	–10

* IEC is International Electrical Engineering Comission.

Table 7. Resistance of dimers **II–IV**, GK, and T-750 to formation of partial discharges (PDs) in an electric field

Parameter	Dimer **II–IV**	GK	T-750
Voltage of PD ignition with apparent charge of 5×10^{-11} C intensity, kV	10.0	9.2	12.5
Gas evolution coefficient, μl J^{-1}	None	275.0	84.0

α-Methylstyrene dimer was prepared by passing α-methylstyrene through a glass column packed with a catalyst and placed in a glycerol thermostat equipped with a heater, a stirrer, and a contact thermometer.

CONCLUSIONS

(1) The use of natural and modified mordenite as catalyst allows preparation of α-methylstyrene dimers with high conversion (up to 71%) and high selectivity (up to 98%).

(2) Linear α-methylstyrene dimers can be used as base components of synthetic transformer oil with high service characteristics and as components of other formulations.

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