# SOME CHARACTERISTICS OF ALKYLATION OF TOLUENE WITH PROPYLENE IN PRESENCE OF ZIEGLER CATALYST

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The alkylation of aromatic compounds with ethylene and propylene proceeds at great speed in the presence of certain complex organometallic catalysts [1]. The system  $TiCl_4 + Al(i-C_4H_9)_2Cl$  (mole ratio of starting reactants Al/Ti = 0.7) studied in the present paper also initiates the alkylation of toluene and benzene. In inert solvents, ethylene forms a high-molecular plastic on this catalyst, while propylene forms liquid oligomers. The common polymerization of these monomers gives true liquid oligomeric copolymers of propylene and ethylene [2]. Consequently, the polymerization of ethylene and the oligomerization of propylene proceed on the same active centers, which differ importantly from the usual cationic centers [2, 3]. This conclusion was based on the results of analyzing the chain structure of the propylene oligomers. The propylene oligomers have a fairly regular chain structure on the type of "head to tail" and contain terminal double bonds. The internal vinylene double bonds are formed by secondary isomerization reactions [3]. The analogous products, synthesized on Friedel-Crafts catalysts, contain almost exclusively internal di- and tri-substituted double bonds [4].

The problem of the present investigation was to study the alkylation of toluene in the presence of  $TiCl_4 + CH_3OH + Al(i-C_4H_9)_2Cl$ , and to compare it with the same reaction when run in the presence of Friedel-Crafts catalysts.

## EXPERIMENTAL METHOD

The alkylation of toluene was run in either liquid propylene or a propylene-propane mixture in high pressure equipment equipped with a stirrer of the propeller type. The reaction rate was checked by the propylene pressure drop employing the Raoult law. See [3] for the method of operating with liquid gases and calculation of the degree of conversion. The toluene was distilled over Na wire, and the CH<sub>3</sub>OH was made absolute and then distilled over CuSO<sub>4</sub>. The unreacted toluene was determined chromatographically. The mean molecular weight of the reaction products  $(\overline{M}_n)$  was found from the condensation heat effects, taking into account the mole fraction of free toluene [5]. The degree of unsaturation was found by the standard method, employing the "bromine numbers." The structure of the reaction products was determined by IR and NMR spectroscopy.

## DISCUSSION OF RESULTS

The propylene oligomers, obtained in the experiments without toluene, contain one double bond [3] (Table 1, Expt. 1). In the presence of toluene the degree of unsaturation of the polymerizate drops to 40%. In harmony with the fractional distillation and IR spectral results, the reaction products are a mixture of unsaturated propylene oligomers and various alkylbenzenes. Modification of the catalyst system by the methanol leads to a sharp increase in the alkylation rate. Here the observed rate constant of propylene

## \*Deceased.

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TABLE 1. TiCl<sub>4</sub> 0.76 g; Al(i-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Cl 0.49 g (Al/Ti = 0.7). In Expts. 3-7 the catalyst is TiCl<sub>4</sub> + CH<sub>3</sub>OH + Al(i-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Cl (CH<sub>3</sub>OH /TiCl<sub>4</sub> = 0.3)

Expt. No.	C7H₃, g	C₃H₅, g	C7H8, mole /liter	C <sub>3</sub> H <sub>6</sub> , mole /liter	°p	αt	K <sub>p</sub> /K <sub>t</sub> •10 <sup>3</sup> , liter /min•g of TiCl4	$\overline{M}_n$	Degree of unsatura - tion, mole %	Āt	Ē
1	0	130	0	9.6	0.93	0	2.5	120	100	_	3
2	73	100	2,04	7.2	0,76	0,21	1,5/0,35	216	40,2		
3	73	100	2,04	7,2	0,94	1,00	18,4	240	5,0	1,92	1,8
4	73	100	2,04	7,2	0,88	0,82	16,5	240	0,3	1,96	1,8
5	16,5	115+10 g С <sub>3</sub> Н <sub>8</sub>	0,54	8,3	0,75	0,67	36/4,5	350	50,5	-	-
6	16,5	115+10 g C₃H₃	0,54	8,3	0,66	0,50	30/5	388	5 <u>4</u> ,5	-	-
7	73	14+86 g C₃H₅	2,04	1	0,92	0,66	15/5	148	2,0	1,4	1,0

<u>Note</u>.  $\alpha_p$  and  $\alpha_t$  are the degrees of propylene and toluene conversion;  $K_p$  and  $K_t$  are the reaction rate constants of propylene and toluene;  $\overline{A}_t$  is the mean degree of toluene alkylation;  $\overline{L}$  is the mean degree of polymerization of the alkyl groups.

consumption increases by practically one order of magnitude  $(16 \cdot 10^{-3} \text{ liter/min} \cdot \text{g of Ti})$ . The fraction of unsaturated products in the formed polymerizate decreases due to the increase in the rate of the alkylation reaction (Fig. 1). For example, the polymerizate from Expt. 4 (see Table 1) consists almost completely of alkylbenzenes (the amount of unsaturated oligomers does not exceed 0.3 mmole).

Two mechanisms can be proposed for the formation of the alkylbenzenes; by reaction with the already formed molecules of the propylene oligomers, which contain vinylidene double bonds that are reactive in cationic processes, or as the result of transfer of the growing chain to toluene, as occurs in telomerization reactions. To ascertain the mechanism of the alkylation reaction we created artificial conditions when the propylene oligomers and toluene were found in the reaction zone in the presence of the catalytically active system. For this in 30 min after the start of reaction (see Table 1, Expt. 6) the unreacted propylene was discharged through a gas meter, a sample was taken from the liquid phase for analysis, and another 0.159 mole of toluene was added to the reactor. In the reactor were found 0.256 mole of toluene (0.097 mole of unreacted toluene and 0.159 mole added after the first stage) and 0.122 mole of unsaturated propylene oligomers with  $\overline{M}_n$  = 388. The reaction of the propylene oligomers with the toluene was run for 2.5 h at 60°C; the amount of free toluene, the mean molecular weight of the reaction products, and the degree of their unsaturation remained unchanged (0.255 mole of toluene, degree of unsaturation 54%, and  $\overline{M}_n = 388$ ). Consequently, the alkylbenzenes are formed only by the reaction of toluene with the growing oligomer chain. The studied catalyst system retains some of the properties of the Ziegler-Natta anionic catalysts. For example. in its presence the propylene oligomers with vinylidene double bonds have a very low reactivity. and consequently do not form a secondary polymerizate [3, 6]. From the cited example it can be seen that double bonds of this type are also unreactive in the alkylation reaction. This conclusion is confirmed by the results of alkylating toluene in the presence of the investigated system using the propylene dimer (2methyl-1-pentene); 2-methyl-1-pentene does not alkylate toluene. Consequently, the mechanism of the investigated reaction is quite different from the mechanism of the same reaction, when run in the presence of the typically cationic Freidel-Crafts catalysts.

From Table 1 it can be seen that the alkylation of toluene proceeds with chain transfer. Thus, for example, in Expt. 4 we obtained 0.615 mole of alkylated toluene derivatives with  $\overline{M}_n = 240$ , while the amount of taken catalyst was  $4 \cdot 10^{-3}$  mole. As a result, at least 150 acts of alkylation took place on each active center (actually it was more, since the catalyst is heterogeneous). The chain transfer in the investigated reaction can be depicted in the following manner:

1) Chain growth: Cat.  $-R + C_3H_6 \rightarrow Cat. -C_3H_6R$ 

2) Chain transfer to propylene and formation of unsaturated oligomer:

$$\begin{array}{c} \text{Cat.-CH}_2\text{--CH}-\text{R}+\text{C}_3\text{H}_6 \rightarrow \text{Cat.-CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_2 = \text{CR} \\ | \\ \text{CH}_3 & | \\ \text{CH}_3 \end{array}$$



Fig. 1. Reaction rate for alkylation of toluene by propylene: 1) control experiment without toluene  $(TiCl_4-Al(i-C_4H_9)_2Cl); 2) TiCl_4-Al(i-C_4H_9)_2Cl, [C_7H_8] = 2.04 mole/liter; 3) TiCl_4-CH_3OH-Al(i-C_4H_9)_2Cl, [C_7H_8] = 2.04 mole/liter; 4) TiCl_4-CH_3OH-Al(i-C_4H_9)_2Cl, [C_7H_8] = 0.54 mole/liter. The curves correspond to Expts. 1, 2, 4, and 5 in Table 1.$ 

Fig. 2. NMR spectrum of fraction with  $\overline{M}_n = 330$  (JNM-C-60HL spectrometer, HMDS).

3) Two variations of chain transfer to toluene are possible:

a) 
$$Cat. -CH_2CHR + C_6H_5CH_3 \rightarrow Cat. H + CH_3C_6H_4CH_2CHR$$
  
 $CH_3$   
b)  $Cat. -CH_2CHC_6H_4CH_3 + C_6H_5CH_3 \rightarrow Cat. -C_6H_4CH_3 + CHC_6H_4CH_3$   
 $CH_3$   
 $CH$ 

The NMR spectra of the obtained alkylbenzenes (Fig. 2) show that the protons of the  $CH_3$  group of toluene do not take part in the chain transfer. Consequently, this variation is not discussed here. To prove the postulated kinetic scheme it is necessary to show that the alkyl substituents contain, besides propyl groups, also substituents that are composed of several monomeric units.

From the NMR data it it possible to calculate the number of protons in the aromatic ring, and correspondingly the number of alkyl groups that had added to toluene as the result of the alkylation reaction. However, in view of the fact that the reaction products are a mixture of alkylbenzenes with a variable number of substituents it is necessary to use the averaged value, the "mean degree of alkylation," which is equal to the ratio of the total number of alkyl groups to the number of alkylbenzene molecules:

$$\overline{A} = \frac{\sum_{i=1}^{p} n_i \cdot i}{\sum_{i=1}^{p} n_i} = \frac{\sum_{i=1}^{p} n_i \cdot i}{N}$$

where  $n_i$  is the number of alkylbenzene molecules with the number of substituents equal to i, i is the number of substituents, p is the maximum possible number of substituents, and N is the number of moles of alkylbenzenes. The values of  $\overline{A}$  lie in the range:  $1 < \overline{A} < p$ . The following ratio is valid for toluene:  $5-\overline{A}_t$  /3 =  $S_1/S_2$ , where  $\overline{A}_t$  is the mean degree of toluene alkylation (for convenience the CH<sub>3</sub> group of the starting toluene is neglected, and consequently  $\overline{A} = \overline{A}_t + 1$ );  $S_2$  and  $S_1$  are the areas of the signals of the protons of the methyl group, attached directly to the aromatic ring, and the protons of the aromatic ring. The proposed equation can be used if the protons of the methyl group of toluene in the alkylation reaction. For example, in the anionic telomerization of ethylene in the presence of organolithium compounds the chain is transferred by the comparatively labile hydrogen atoms of these groups have a characteristic NMR signal, which is absent in the spectra of the protons of the investigated reaction. Consequently, chain transfer is accomplished only by the protons of the aromatic ring and the proposed equation

TABLE 2

	I	$\overline{M}_n$	1	Mole fraction, %			
Expt. No <b>:</b>	Fraction No.		fraction of unsaturated of toluene in compounds fraction		Āt	Ĺ	
	<u> </u>	02	42.7	9	9		
2		92	46 6	53	47		-
	3	121	16,3	5	92	_	-
	4	176	8,1	40	0	-	-
	5	204	0,8	50		4 07	-
	6 7	220 388	3.3 11,1	53 70	0	1,97	_
4	1 1	92	14	0,2	99,8		-
-	$\hat{2}$	93	2,5	10,8	82		-
	3	132	3,2	0	32	1,05	1
	4	180	29,5	0	0	4 00	1 50
	5	208	26,1			1,85	1,52
	1 6	330	26,4	1 0		ι <i>4,9</i> μ	1 1,00

\*The experiment number corresponds to Table 1.

can be used to determine  $\overline{A}$ . In combination with  $\overline{M}_n$  this parameter makes it possible to determine the average length of the alkyl substituents. For the light fractions,  $\overline{A}_t \approx 1$  (see Table 1, Expt. 7). For the comparatively high-molecular fractions,  $\overline{A}_t$  increases up to 2.9-3 (i.e., three other alkyl substituents are present besides the methyl group). The alkyl chainlets of these products consist of several monomeric units. For example, in the fraction with  $\overline{M}_n = 330$  (Table 2, Expt. 4),  $\overline{A}_t = 2.9$  and  $\overline{L} = 1.95$ , i.e., the components are mainly dimers, while in the fraction with  $\overline{M}_n = 580$ , which could be isolated from the alkylben-zenes (Expt. 3), the alkyl groups consist of four monomeric units ( $\overline{A}_t = 3$ ). The information on the length of the alkyl substituents can be regarded as being proof that the chain growth reaction exists in the studied process and as evidence that the proposed kinetic scheme is valid.

The experimental results make it possible to determine the value of the ratio of the rate constants of chain transfer to toluene and propylene. The mole fraction of the unsaturated propylene oligomers in the reaction products is determined by the following equation:

$$\beta = \frac{K_{\rm p} {}^{\rm p} C_{\rm p}}{K_{\rm p} {}^{\rm p} C_{\rm p} + K_{\rm p} {}^{\rm t} C_{\rm t}}$$

where  $K_p^p$  and  $K_p^t$  are the rate constants of chain transfer to toluene and propylene, and  $C_t$  and  $C_p$  are respectively the toluene and propylene concentrations ( $C_t = 2 \text{ moles/liter}$ ,  $C_p = 5 \text{ moles/liter}$ , and  $\beta = 0.003$ , see Table 1, Expt. 4).

As a first approximation the change in the toluene concentration can be neglected, since the disubstituted benzenes are also chain transfer agents. The ratio  $K_p^t/K_p^p = 10^3$ . The reactivity of toluene as a chain transfer agent is strongly dependent on its active concentration. When  $C_t = 0.54$  mole/liter the ratio  $K_p^t/K_p^p$  drops to 4, and a similar relation is observed in a number of ionic telomerization processes [7]. It is entirely possible that one of the reasons, responsible for the decrease in the reactivity of toluene, in the experiments with  $C_t = 0.54$  mole/liter is the formation of inhomogeneous active centers.

The isomeric composition of the alkylbenzene fraction with  $\overline{M}_n = 140$  (see Table 1, Expt. 7) was established from the IR spectra. The absorption coefficients in the 670-900 cm<sup>-1</sup> region (vibrations of C-H bonds of benzene ring) were determined from the spectra of the pure cymenes. On the basis of the NMR and IR spectral data it was established that the fraction with  $\overline{M}_n = 140$  is a mixture of the o-, m-, and p-cymenes (respectively 34, 28, and 38%). A product of approximately the same composition is also formed in the presence of the typically cationic Friedel-Crafts catalysts [8]. Nevertheless, important differences exist between these reactions.

- Olefins with vinylidene double bonds do not alkylate toluene in the presence of the investigated system. The low reactivity of this type of olefins is characteristic for coordination-anionic Ziegler -Natta catalysts.
- 2) In the studied reaction the alkylation of toluene is the result of chain transfer to the toluene. Cymene is the first monomeric link that is formed in the transfer of the growing chain. Transfer to subsequent links leads to the formation of alkyl chainlets, which consist of several monomeric units.

The data on the structure of the alkyl substituents, obtained from an analysis of the NMR spectra, enable making some conclusions regarding the mechanism of the formation of the alkyl chainlets. Chain transfer to toluene proceeds in harmony with reaction (3b) of the kinetic scheme, since reaction (3a) leads to the formation of the methylene group, which is shielded by the aromatic ring. Such groupings have a characteristic signal in the  $\delta$  2.4 region, which is absent in the spectra of the obtained alkylbenzenes. The cymenes, which are formed in substantial amounts in the experiments with a propylene concentration of 1 mole/liter and are present in the light fractions of the products, obtained in all of experiments testify to the fact that the addition of the first monomeric unit is accompanied by the formation of the isopropyl group.

In our opinion, the observed relation between the length of the alkyl substituents and the propylene concentration (see Table 1, Expts. 4 and 7) is additional proof of the chain growth reaction.

If each chainlet contains a methine group, shielded by the aromatic group, then the following equation should be fulfilled with an accuracy up to the errors of measurement:

$$S_{3}/S_{2} = \bar{A}_{t}/3$$

where  $S_3$  is the absorption area of the signal of the protons of the methine groups, attached directly to the aromatic ring. Actually, for various fractions the ratio  $S_3/S_2$  is some 20-37% smaller than the calculated value (error  $\pm 5\%$ ). Consequently, ~30% of the chainlets contain a quaternary carbon atom, which is directly attached to the aromatic ring. Chain transfer to toluene leads to the formation

## CH<sub>3</sub> CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> CH<sub>3</sub>

of products, the structure of which was proved by an analysis of the NMR spectra. Each substituent contains only one terminal methyl

#### $CH_3C_6H_4CHCH_2CH_2CH_3$ $\downarrow$ $CH_3$

group, each which follows from an analysis of the fraction with  $\overline{M}_n = 330$ ,  $\overline{A}_t = 2.9$  (see Table 2, Expt. 4). For these alkylbenzenes the mean length of the substituents is equal to 1.95 monomeric units. The structure of the terminal groups of the alkyl substituents was established from the intensity of the peaks in the region  $\delta = 0.8-0.9$ , where the protons of the CH<sub>3</sub> groups, not shielded by the aromatic ring, absorb. The ratio between such terminal CH<sub>3</sub> groups and the CH<sub>3</sub> groups of toluene is determined by the equation

$$S_2/S_4 = 3/B$$

where  $S_4$  and B are respectively the absorption area of the signal of the protons of the "terminal"  $CH_3$ groups and the average number of protons in them; B = 7.3 for the fraction with  $M_n = 330$ . Assuming  $A_t = 2.9$ , the number of protons of the "terminal"  $CH_3$  groups, that belong to each alkyl chainlet, is 2.5. Consequently, each alkyl chainlet contains only one  $CH_3$  group that is not shielded by the benzene ring. Reaction (3b) makes it possible to explain the formation of the structural groupings that are detected spectrally. The other possible mechanism of chain transfer to toluene, with the formation of the intermediate reactive hydride, is not very probable, since it does not exclude the possibility of forming methylene groups that are attached directly to the aromatic ring [reaction (3a)]. The structure characteristics of the comparatively long alkyl substituents can be explained if it is assumed that inversion occurs when the propylene adds in the chain growth reaction, and isomerization processes that are characteristic for cationic reactions take place.

$$\begin{array}{c} CH_{3} \\ Cat. - CH_{2}CH - C_{6}H_{4}CH_{3} \underbrace{\begin{array}{c} C_{3}H_{6} \\ Growth \end{array}}_{CH_{3}} \xrightarrow{C_{3}H_{6}} (30\%) \\ \downarrow & \downarrow \\ CH_{3} \\ \end{array} \xrightarrow{C} Cat. - CHCH_{2}CC_{6}H_{4}CH_{3} (30\%) \\ \downarrow & \downarrow \\ CH_{3} \\ \hline CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ \end{array} \xrightarrow{C} Cat. - CHCH_{2}CH_{2}CH_{2}CH_{6}H_{4}CH_{3} (70\%) \\ \downarrow & \downarrow \\ CH_{3} \\ CH_{3} \\ \hline CH_{3} \\ \end{array}$$

In the investigated reaction (the same as in the reactions run in the presence of Friedel-Crafts catalysts) the protons of the aromatic ring are reactive. The difference consists in the fact that the chain growth reaction is expressed quite clearly when the alkylation of toluene is run on the complex catalyst. These facts make it possible to classify the studied reaction as being the cationic telomerization of propylene. In harmony with the table given in review [9] for the properties of Ziegler catalysts, the proposed mechanism for the growth of alkyl chainlets is coordination-cationic.

The coordinating effect of the ion of the transition metal, entering into the composition of the active center, is manifested in a retention of the reactivity of olefins that is characteristic for catalysts of the Ziegler series. Propylene, a monomer with a vinyl double bond, has the maximum reactivity. The olefins with vinylidene double bonds do not alkylate toluene.

## CONCLUSIONS

1. The alkylation of toluene in the presence of the complex organometallic catalyst:  $TiCl_4 + Al(i-C_4H_9)_2Cl + CH_3OH$  is the consequence of the cationic telomerization of propylene.

2. A method was proposed for determining the mean degree of alkylation and the structure of the reaction products was studied.

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