Kinetic Study on Competitive Alkylation of an Arene Mixture Coming from the Petrochemical Industry

LUCIA ODOCHIAN[1], CAMELIA SOLDEA[2], CRISTINA PAIUS[1], ANCA MIHAELA MOCANU[2], COSTEL MOLDOVEANU[1]
[1] University " Al. I. Cuza" , Faculty of Chemistry, 11 Blv. Carol I, 700506, Iaşi, Romania
[2] Technical University "Gh.Asachi" Iasi, Faculty of Chemical Engineering, 71A D. Mangeron, Ave., 70050-Iasi, Romania

In the present paper the kinetics of the competitive Friedel-Crafts alkylation of a mixture of xylene isomers and ethylbenzene with t-buthyl chloride and anhydrous $AlCl_3$ as a catalyst were studied by using a petrochemical by-product(Petrochemical Company of Brazi), under the optimum conditions of obtaining the alkylated products under consideration. The concentrations of the rection major components were estimated by gas-chromatography. The kinetic parameters of the competitive alkylation were estimated and the following reactivity series of the mixture components settled:

$$k_{o\text{-}xylene} > k_{ethylbenzene} > k_{m\text{-}xylene}$$

although the calculated corresponding activation energies obeyed the following order:

$$E_{a\ m\text{-}xylene} < E_{a\ o\text{-}xylene} < E_{a\ ethylbenzene}$$

The reactivity was made evident to be strongly influenced by the steric factor (p) of the alkylation reactions which was calculated and the following series found:

$$p_{m\text{-}xylene} < p_{o\text{-}xylene} < p_{ethylbenzene}$$

Since the reaction thus performed resulted in alkylated m-xylene as the major reaction product which could be separated by distillation in a high purity state, the fact has to be pointed out that the present study brings an important contribution both to the high capitalization of the petrochemical by-product and to the obtaining of 5-t-buthyl-m-xylene of high quality as a key intermediate in nitro musk syntheses.

Keywords: xylenes, Friedel-Crafts alkylation, optimum conditions, kinetical parameters, by-product capitalization

The obtaining of great majority of the products to be used in various fields of human activity–drugs, dyes, pesticides, cosmetics, household products etc- is greatly based on the processing of aliphatic and aromatic hydrocarbons [1].

By applying the proper conditions of their transformations at both laboratory and industrial scale,the aromatic hydrocarbons can be submitted to oxidative [2, 3] and hydrogenation [4, 5] processes or electrophilic substitutions [6, 7], affording final products as well as intermediates for products of important uses.

The petroleum, one of the main sources of raw materials for the chemical industry, offers also products and by-products suitable for being further processed to useful products. In this connection, the xylene mixture resulting as a by-product from the Romanian petrochemical industry might be taken as a good example as a promising material to be properly studied and capitalized. Its approximate composition is the following: ethylbenzene (9.42%), *p*-xylene (23.80%), *m*-xylene (62.98%), *o*-xylene (3.80%) [8].

The main constituent of this mixture, *m*-xylene, is an important raw material for the organic synthesis products, the nitro musks among them: xylene musk, ketone musk, thibetin musk. The pure *m*-xylene used as a starting raw material in these syntheses involves rather high prices while its replacement by the by-product of the petrochemical industry might result in significant price lowering. The rather close boiling points of the xylene isomers do not allow a good separation of the mixture components.

Japanese scientists [9] have separated the *m*-xylene by alkylation, followed by the product separation and final dealkylation to the pure *m*-xylene.

The main intermediate for obtaining the nitro musks, 5-*t*-buthyl-*m*-xylene, may be successfully synthesized by performing a selective Friedel-Crafts alkylation of the xylene mixture coming from the petrochemical industry giving up the separation of pure *m*-xylene, b.p.=199.5°C.

The optimum alkylation conditions allowing high yields and quality indices of the 5-t-buthyl-m-xylene, were studied in previous papers and patents describing experiments made with various alkylating agents (*t*-buthylic alcohol, *t*-buthyl chloride, isobutene) and catalysts (anhydrous $AlCl_3$, $FeCl_3$, molecular sieves, zeolites) [10 - 14].

The optimum parameters of the alkylation of *m*-xylene in the isomer mixture by means of *t*-buthyl chloride, with anhidrous $AlCl_3$ and $FeCl_3$, respectively, were established in previous papers [8, 14] and taken subsequently in the kinetic study of this reaction under the mentioned experimental conditions [15].

In the present paper a kinetic study on the competitive alkylation of the components in the petrochemical by-product by *t*-buthyl chloride and with anhidrous $AlCl_3$ as a catalyst is reported.

Experimental part

Experimental equipment

The kinetic study of the xylene mixture alkylation was performed in an installation consisting of a three-neck flask provided with an electric stirrer, thermosetting jacket, termometer, refrigerator, gase outlet connection.

Working procedure

The mixture consisting of xylene isomers and ethylbenzene and the catalyst are placed in the reaction flask. The newly synthesized t-buthyl chloride of 98% purity

* email: lodochian@yahoo.com

is then added dropwise from the dropping funnel. The time when the *t*-buthyl chloride addition was over was considered as the initial reaction time, at a constant temperature (0, 10, 40°C).

Reaction mixture samples (0,8 μL) were taken off at equal time intervals and injected into the chromatographic column. The reaction time was of 3 - 6 h function of temperature.

Analysis of mixture

The reaction mixture was analysed by gas-chromatography. The Pye chromatograph, series 104, model 34 was provided with a thermal conductivity detector. The glass chromato-graphic column of 1.5 m length and 4 mm diameter had a filling of chromosorb WAV (60 - 80 Mesh Benton (34.5%) and dodecylphthalate (5%) as recommended for separating components of such type [16].

The chromatograms were recorded under the following conditions: column temperature – 70^0 C, bridge current – 50 mA, sensitivity – 10, gas carrier – argon, argon flowrate – 20 cm^3/min.

Under these conditions the separation of the major components was good and their identification was made based on the retention times for the pure components: ethyl-benzene – 3.2 min, *o*-xylene – 4 min, *m*-xylene – 5.1 min, *p*-xylene – 6 min, *t*-buthyl chloride – 1.2 min, alkylated ethylbenzene – 9.5 min, alkylated *o*-xylene – 4.3 min, alkylated *m*-xylene – 15.3 min.

In figures 1 and 2 the chromatograms for the mixture of xylenes and ethylbenzene in a by-product mixture coming from the petrochemical industry (Brazi) as well as for the alkylated products and *t*-buthylchloride are drawn. A good separation of the components can be noticed.

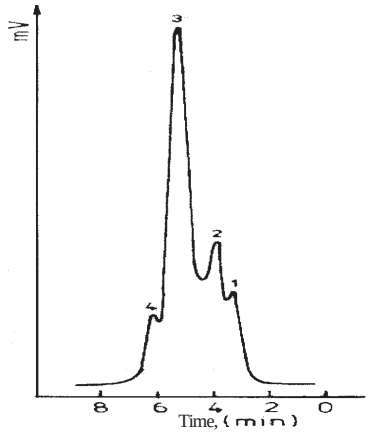


Fig. 1. Chromatogram of a xylenes – ethylbenzene mixture, a by-product of the petrochemical industry (Petrochemical Company of Brazi) 1 – ethylbenzene, 2 – o-xylene, 3 – m-xylene, 4 – p-xylene

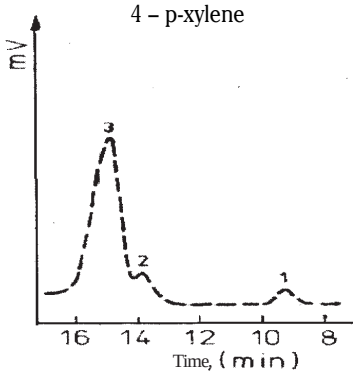


Fig. 2. Chromatogram of a alkylated mixture 1 – alkylated ethylbenzene, 2 –alkylated o-xilen, 3 – alkylated m-xilen

Optimum Conditions of the Alkylation Reaction

The optimum reaction condition were settled by studying the influence of the main parameters[8, 14]:

- substratum/alkylating agent mole ratio, between 1/1 – 6/1;
- catalyst nature and amount: anhydrous $AlCl_3$;
- alkylating agent/ catalyst mole ratio, between între 1/ 0,1 – 1/0,3;
- temperature, between 0 – 10°C;
- reaction time: 2 – 6 h

and the found optimum conditions were:

- substratum/alkylating agent mole ratio: 4/1
- alkylating agent/catalyst mole ratio 1/0,1
- temperature: 0 – 10°C
- reaction time: 2 – 4 h

Results and discussion

The mixture of xylenes and ethylbenzene in the petroleum by-product (Petrochemical Company Brazi) taken in the present study had the following composition: 3,93% ethyl-benzene, 3.93% *o*-xylene, 70.89% *m*-xylene, 21,23% *p*-xylene.

For the optimum reaction conditions under which the kinetic study was performed, namely the substratum (xylene mixture)/alkylating agent/catalyst mole ratio = 4/ 1/0.1 the corresponding amounts were: 300 mL substratum (d = 0.8641 g/cm)/65 mL *t*-buthyl chloride (d = 0.851 g/cm)/ 6.5 g anhydrous $AlCl_3$.

Under these conditions the initial concentrations of the substratum components were:

$c_{0\ \text{ethyl-benzene}} = 0.254$ mol/L

$c_{0\ m\text{-xylene}} = 4.59$ mol/L

$c_{0\ o\text{-xylene}} = 0.254$ mol/L

$c_{0\ p\text{-xylene}} = 1.37$ mol L

The major components of the reaction were dosed by gas chromatography at the temperatures of 0, 10, 40°C.

As revealed by figure 3, the reaction components were well separated.

Tables 1-3 present the concentrations at different reaction times, obtained by gas chromatographical analysis of the reagents (ethyl-benzene, *o*-xylene and *m*-xylene) on the basis of the standard curves given in figure 4a, b.

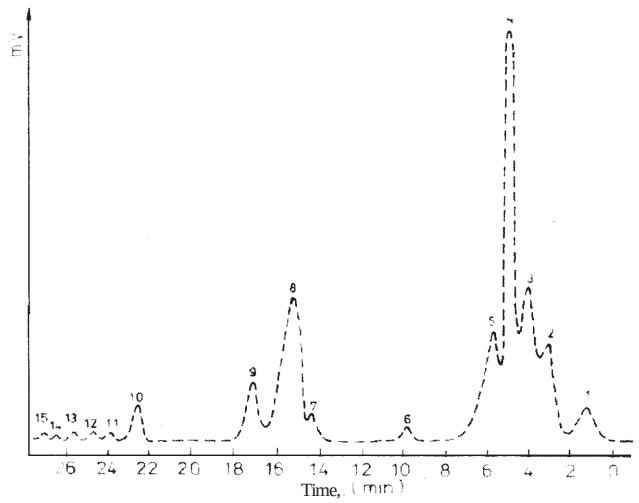
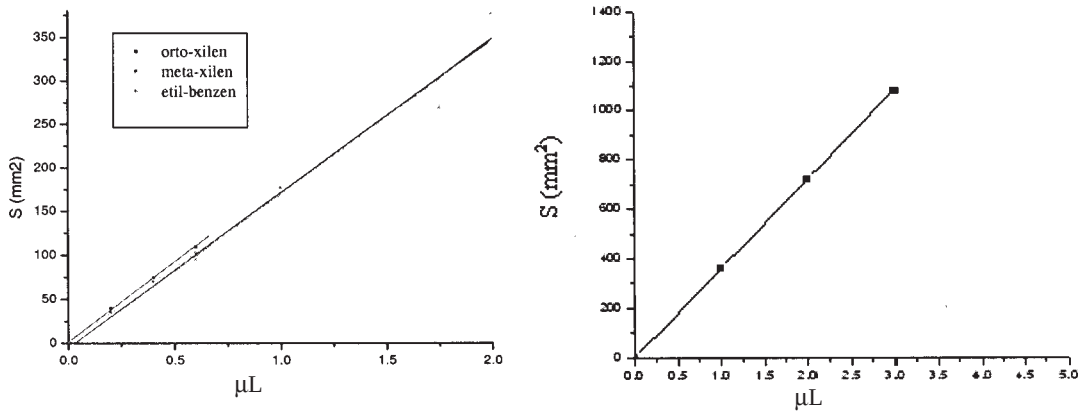


Fig. 3. Chromatogram obtained under optimum reaction condition with $AlCl_3$ as a catalyst at reaction time of 30'(10°C) 1 – t-butyl chloride, 2 – ethylbenzene, 3 – o-xylene, 4 – m-xylene, 5 – p-xylene, 6 – alkylated ethylbenzene, 7 –alkylated o-xylen, 8 – alkylated m-xylen, 9-15 – unidentified components



a b

Fig. 4. Standard curve (a) – m-xylen, o-xylen, ethylbenzene (b) – alkylated m-xylen

Table 1
REAGENT CONCENTRATIONS IN TIME, AT 0°C

Time (min)	0	20	40	60	80	100	120	140	160	200
$C_{ethyl\text{-}benzene}$ (mol/l)	**0.254**	0.2	0.175	0.155	0.142	0.125	0.11	0.105	0.094	0.093
$C_{o\text{-}xylene}$ (mol/l)	**0.254**	0.197	0,155	0.12	0.1	0.09	0.087	0.086	0.086	0.086
$C_{m\text{-}xylene}$ (mol/l)	**4.59**	3.54	3.00	2.87	2.5	2.35	2.20	2.00	2.00	2.00

Table 2
REAGENT CONCENTRATIONS IN TIME, AT 10°C

Time (min)	0	20	40	60	80	100	120	140	160	200
$C_{ethyl\text{-}benzene}$ (mol/l)	**0.254**	0.175	0.1475	0.13	0.112	0.1	0.0985	0.097	0.097	0.0965
$C_{o\text{-}xylene}$ (mol/l)	**0.254**	0.165	0.120	0.09	0.080	0.075	0.074	0.0735	0.0735	0.0735
$C_{m\text{-}xylene}$ (mol/l)	**4.59**	3.4	2.80	2.5	2.3	2.1	1.9	1.73	1.73	1.75

Table 3
REAGENT CONCENTRATIONS IN TIME AT 40°C

Time (min)	0	20	40	60	80	100	120	140	160	200
$C_{ethyl\text{-}benzene}$ (mol/l)	**0.254**	0.15	0.116	0.087	0.068	0.067	0.067	0.073	0.074	0.074
$C_{o\text{-}xylene}$ (mol/l)	**0.254**	0.145	0.083	0.062	0.042	0.030	0,030	0.028	0.028	0.028
$C_{m\text{-}xylene}$ (mol/l)	**4.59**	2.9	2.45	2.0	1.8	1.6	1.4	1.3	1.3	1.3

The p-xylene concentration was not found to change in time.

The kinetic curves for the reagents by means of the data in tables 1-3 are depicted in figure 4- 6.

The kinetic parameters *n* and *k* were estimated under the presumtion of an alkylation rection of the 2nd order [7] and, by means of the kinetic curves, the half-life time, t ½, was determined which allows the estimation of the rate constant based on the characteristic equation $k = 1 / c_o t_{1/2}$ (1) at the three temperatures [17a].

The values of t1/2 and k for the alkylation reaction of *o*-xylene, ethylbenzene and *m*-xylene at 0, 10 şi 40°C are given in table 4.

The data in table 4 indicate the following series of the reactivities of these reagents towards *t*-buthyl chloride under the optimum reaction conditions [7].

$$k_{o\text{-}xylene} > k_{ethylbenzene} > k_{m\text{-}xylene}$$

The reactivity of the *o*-xylene, ethylbenzene and *m*-xylene towards *t*-buthyl chloride with anhydrous $AlCl_3$ as a catalyst may be explained by taking the fact into account that these alkylation reactions are developing according to the electrophilic substitution mechanism on a substituted aromatic ring containing pre-existing substitutes of the I-st order. The aromatic ring is thus only slightly activated and the new sustitutes are directed to the ortho and para positions. The orientation of the aromatic electrophilic substitution is also influenced by the bulky electrophilic reagent (ER). The ER (*t*-buthyl carbocation) is a bulky group causing the steric hindrance with the pre-existing substitutes.

Since the steric hindrances are of maximum values with the substitutes in the nearest positions *(ortho* position), the alkyl group can be directed in the *para* position only.

The analysis thus made affords the following conclusions:

- the alkylation of *p*-xylene with *t*-buthyl chloride does not develop or develops at a very low, unsignificant rate.
- the reaction with *m*-xylene involves a site deactivated by the pre-existing substitutes (*meta*) so that the reaction rate will be lower.

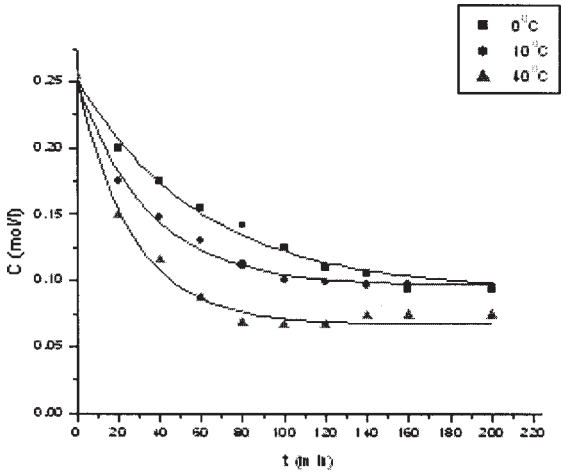


Fig. 5. Kinetic curve of ethylbenzene at 0°C, 10°C and 40°C

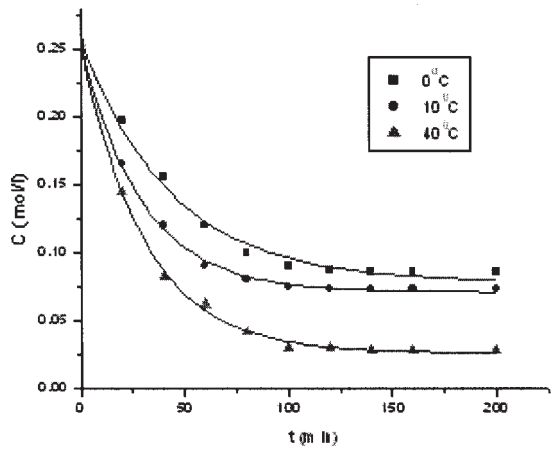


Fig. 6. Kinetic curve of ortho-xylene at 0°C, 10°C and 40°C

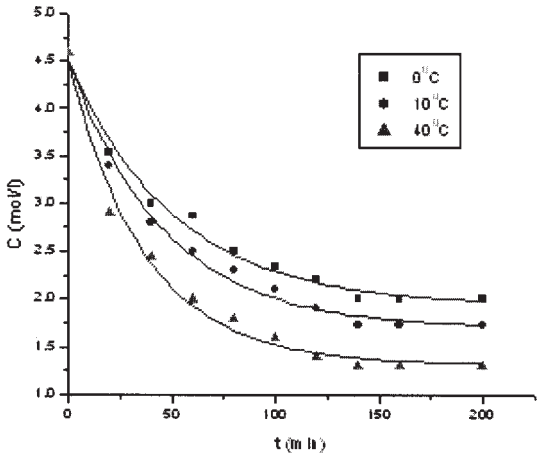


Fig. 7. Kinetic curve of metha-xylene at 0°C, 10°C and 40°C

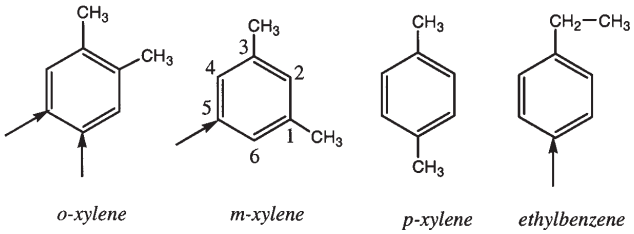


Fig. 8. Components of the starting mixture

- the reaction with *o*-xylene and ethylbenzene takes place in a site activated by the pre- existing substitutes which results in a reaction rate higher than with *m*-xylene;
- from kinetical point of view these aspects must be reflectd by the sterical factor value (p).

In order to estimate the energy of activation (Ea) and the pre-exponential factor (A) of the alylation reactions, the reaction rates were determined by numerical differentiation for a reaction time of 40 min. and the three temperatures. In table 5 the data required for applying the

Table 4
HALF-LIFE TIMES AND RATE CONSTANTS FOR THE ALKYLATION REACTION OF o-XYLENE, ETHYL-BENZENE AND m-XYLENE AT 0°C, 10°C, 40°C

Temperature	*o*-xylene		ethyl-benzene		*m*-xylene	
	$t_{1/2}$ (min)	k $(mol^{-1} \cdot l \cdot s^{-1})$	$t_{1/2}$ (min)	k $(mol^{-1} \cdot l \cdot s^{-1})$	$t_{1/2}$ (min)	k $(mol^{-1} \cdot l \cdot s^{-1})$
0°C	56	1.17×10^{-3}	92	7.13×10^{-4}	110	3.3×10^{-5}
10°C	34	1.93×10^{-3}	64	1.025×10^{-3}	84	4.22×10^{-5}
40°C	20	3.28×10^{-3}	23	3.85×10^{-3}	50	7.262×10^{-5}

Table 5
NECESSARY DATA FOR DRAWING THE REACTION RATE DEPENDENCE ON TEMPERATURE AT A REACTION TIME OF 40 MIN

Temperature (K)	Reagent	273	283	313
$\frac{1}{T} K^{-1}$	-	$3{,}66 \times 10^{-3}$	$3{,}53 \times 10^{-3}$	$3{,}19 \times 10^{-3}$
$v_{40'}$ $mol \cdot l^{-1} \cdot s^{-1}$	ethyl-benzene	1.0×10^{-3}	1.313×10^{-3}	2.40×10^{-3}
	o-xylene	1.75×10^{-3}	2.0×10^{-3}	3.1×10^{-3}
	m-xylene	2.0×10^{-2}	2.5×10^{-2}	3.25×10^{-2}
ln $v_{40'}$	ethyl-benzene	-6.9	-6.63	-6.04
	o-xylene	-6.35	-6.22	-5.78
	m-xylene	-3.91	-3.70	-3.43

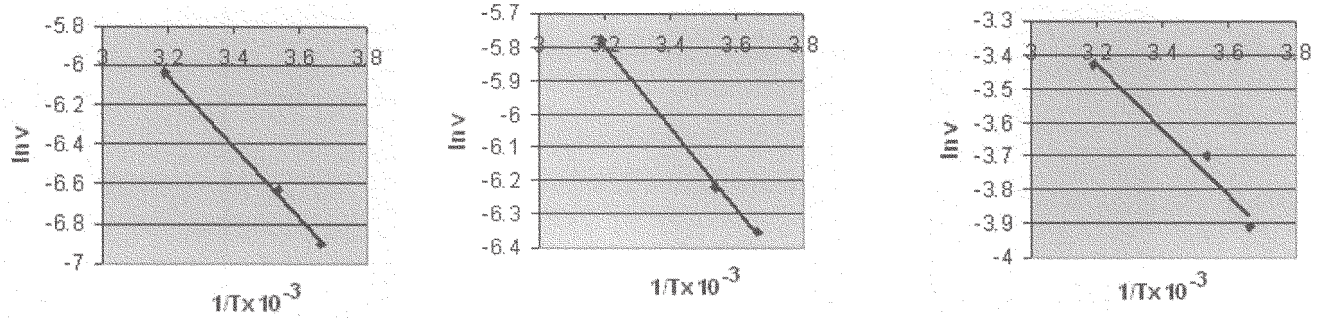


Fig. 9. ln v = f(t) dependence at 40': a) ethylbenzene, b) o-xylene, c) m-xylene

Table 6
NECESSARY DATA FOR DRAWING THE REACTION RATE CONSTANT VERSUS TEMPERATURE

Temperature (K)	Reagent	273	283	313
$\frac{1}{T} K^{-1}$	-	3.66×10^{-3}	3.53×10^{-3}	3.19×10^{-3}
k $mol^{-1} \cdot l \cdot s^{-1}$	ethyl-benzene	7.13×10^{-3}	1.03×10^{-3}	2.86×10^{-3}
	o-xylene	1.17×10^{-3}	1.93×10^{-3}	3.3×10^{-3}
	m-xylene	3.3×10^{-2}	4.22×10^{-2}	7.26×10^{-5}
ln k	ethyl-benzene	-7.25	-6.88	-5.86
	o-xylene	-6.75	-6.25	-5.72
	m-xylene	-10.32	-10.1	-9.53

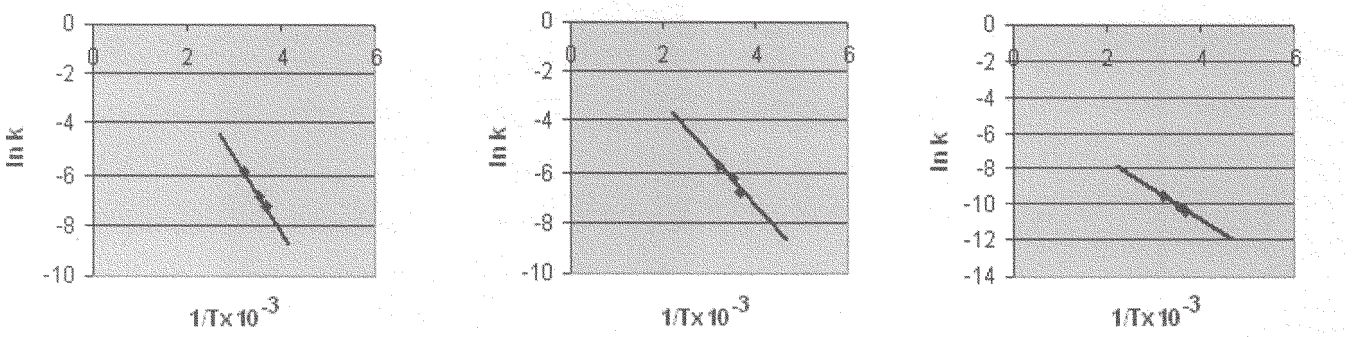


Fig. 10. ln k = f(t) dependence: a)ethylbenzene, b) o-xylene, c) m-xylene

Table 7
ENERGIES OF ACTIVATION (KJ/MOL) OF THE ALKYLATION REACTIONS OF ETHYLBENZENE, O-XYLENE AND M-XYLENE

	ethyl-benzene	*o*-xylene	*m*-xylene
$v_{40'}$ = **f (T)** ecuația (V.2.1)	18.07	15.58	13.16
k = f (T) ecuația (V.2.2)	25.516	19.09	14.66

Arrhenius equation dependence of the reaction rate on temperature are given:

$$\ln v = \ln cst - \frac{Ea}{R} \cdot \frac{1}{T} \quad (2)$$

In figure 9 a, b, c the Arrhenius dependence v = f(T) according to the equation (2), for the three reagents is drawn.

In table 6 the data necessary for drawing the dependence of the reaction rates on temperature according to the linearized Arhhenius equation are given

$$\ln k = \ln A' - \frac{Ea}{R} \cdot \frac{1}{T} \quad (3)$$

and the dependence obtained graphically in figure 10 a,b,c.

The obtained values of the energies of activation are listed in table 7.

As made evident by data in table 7 the alkylation activation energy with anhydrous $AlCl_3$ as a catalyst, is lower with *m*-xylene than with *o*-xylene and ethylbenzene, according to the following series:

$$E_{a\ m\text{-}xylene} < E_{a\ o\text{-}xylene} < E_{a\ ethylbenzene}$$

although the reaction rates obey the series:

$$k_{o\text{-}xylene} > k_{ethylbenzene} > k_{m\text{-}xylene}$$

This apparently strange finding reveals the significance of the steric factor as regards the reactivity of the three reagents towards *t*-buthyl chloride allowing the estimation of the steric factor for the reactions under study at the three temperatures [17b].

The theoretical correlation is well-known:

Table 8
VALUES OF A' AND P FOR THE THREE ALKYLATION REACTION AT 0°C, 10°C AND 40°C

	T° C	ethyl-benzene	*o*-xylene	*m*-xylene
Ea (Kj/mol)	-	21.84	17.34	13.91
A' $mol^{-1}\ l\ s^{-1}$	0^0 C	$1.5\cdot10^{1}$	2.56	$1.5\cdot10^{-2}$
	10^0 C	$1.07\cdot10^{1}$	3.00	$1.56\cdot10^{-2}$
	40^0 C	$1.66\cdot10^{1}$	2.56	$1.52\cdot10^{-2}$
p	0^0 C	$1.053\cdot10^{-7}$	$2.56\cdot10^{-8}$	$1.50\cdot10^{-10}$
	10^0 C	$1.07\cdot10^{-7}$	$3.00\cdot10^{-8}$	$1.56\cdot10^{-10}$
	40^0 C	$1.261\cdot10^{-7}$	$2.56\cdot10^{-8}$	$1.52\cdot10^{-10}$

$$k = p \cdot Z_{AB}{}^{0} e^{-Ea/RT} \quad (4)$$

where:

p – steric factor (0-1);

Z^{o}_{AB} - specific number of collisions , being of about 10^8 mol for the bimolecular reactions;

Ea – activation energy Kj/mol;

T – temperature, K;

R – universal constant;

and

$$k = A' e^{-Ea/RT} \quad (5)$$

where the pre-exponential factor A' is given by the relationship:

$$A' = p \cdot Z^{0}_{AB} \quad (6).$$

In table 8 the values of the pre-exponential factor, A', and steric factor, p, for the three alkylation reactions at 0, 10 and 40°C are given.

It follows that the steric factor for the alkylation of m-xylene is of about 10^{-10}, much lower than with ethyl-benzene (10^{-7}) and *o*-xylene (10^{-8}) which results in a much lower rate constant although the activation energy is lower. The obtained steric factors are in agreement with the previous explanations on the reactivity of these reagents towards *t*-buthyl chloride.

Conclusions

The kinetic study on the Friedel-Crafts alkylation of the mixture of xylene isomers and ethylbenzene with *t*-buthyl chloride affords the following conclusions:

- by means of the applied procedure the *m*-xylene in the petroleum by-product mixture containing xylene isomers and ethylbenzene is highly capitalized;
- the 5-*t*-buthyl-*m*-xylene of a high purity is obtained and easily separated by distillation due to the different boiling points of the mixture components, this intermediate leading to nitro musks of high purity and quality;
- low power consumption in virtue of the middle alkylating temperatures;
- the possibility of using the remaining hydrocarbon mixture as a dissolver to the same purposes as the starting hydrocarbon mixture;
- the rate constants of the alkylation reactions obey the series given below

$$k_{o\text{-}xylene} > k_{ethylbenzene} > k_{m\text{-}xylene}$$

which reflects properly the reactivities of *o*-, *m*-, *p*-xylene and ethyl-benzene towards *t*-buthyl chloride under the optimum reactions conditions with anhydrous $AlCl_3$ as a catalyst;

- the temperature raising promotes the alkylation to 5-*t*-buthyl-*m*-xylene within the 0 – 40°C temperature range, the reaction being of the Arrhenius type. At higher temperatures other reactions are also able to proceed which diminish the yield of the main alkylation product.
- the activation energies obey the following order:

$$E_{a\ m\text{-}xylene} < E_{a\ o\text{-}xylene} < E_{a\ ethylbenzene}$$

the temperarure influence being characteristic of every reaction under the applied working conditions. The lower activation energy of the reaction leading to 5-*t*-buthyl-*m*-xylene would explain the selective alkylation of *m*-xylene in the mixture of ethylbenzene and xylenes.

References

1.GHEGAN, I., IONESCU, S.F., OPRIŞ, I. „Ingineria prelucrării hidrocarburilor", Editura Tehnică, Bucureşti, 1999

2.NICOLAE, A., MARIA, Gh., Rev. Chim. (Bucuresti), **58** , no. 4 , 2007, p. 427

3. GHEGAN, I., IONESCU, S.F., OPRIŞ, I., Rev. Chim. (Bucuresti), **54,** no.3, 2003, p. 71

4. JUGANARU ,T, IONESCU, CT, BOMBOS, D, BOMBOS, M, MATEI, V, Rev. Chim. (Bucuresti), **58,** no.10, 2007, p.983

5. JUGANARU, T., IONESCU, CT., BOMBOS, D., BOMBOS, M., MATEI, V., Rev. Chim. (Bucuresti), **58,** no. 7, 2007, p 698

6.LUPUŞOR, G., MERICĂ, E., ŞOLDEA, C., Ingineria sintezei intermediarilor aromatici, Baze teoretice, **I**, Editura Tehnică, Bucureşti, 1977

7. LUPUŞOR, G., MERICĂ, E., ŞOLDEA, C., Ingineria sintezei intermediarilor aromatici, Procese fundamentale, **II**, Editura Tehnică, Bucureşti, 1981

8. MERICĂ, E., ŞOLDEA, C., ODOCHIAN, L., PETRESCU, M., Volumul Simpozionului „Contribuţia cercetării şi proiectării din institutele de învăţământ superior la reducrea consumului de materii prime, combustibil, energie", Galaţi, aprilie 1983, p. 275

9. SHIMADA, K., NAGAHAMA, S., Express Informatica, Prom. Org. Sintey, **42**, 1975, p. 10

10. GRIGORI A. SERADA, VIKUL B. RAJPARA, J. Chem. Ed., **84,** nr. 4, 2007, 692

11. SHINAE, JUN, RYONG, RYOO, J. of Catalysis, **195**, 2000, 237

12. JANSEN, J.C., CREYGHTON, E., NIJO, S. L., VAN KANIGSVELD, H., Catal. Today, **38**, 1997, p.205

13. LLOPIS, F.T., SASTRE, G., CORMA, A., J. of Catalysis, **227**, nr.10, 2004, p.227

14. ŞOLDEA ,C., MERICĂ, E., ODOCHIAN, L., PETRESCU, M., Brevet R.S.R., 85986/1983

15. ŞOLDEA, C., MERICĂ, E., ODOCHIAN, L., Daniliuc M., Păiuş C.M., RSCC magazine, **7,** nr.4, 2007, p. 41

16. VASILE, C., ODOCHIAN, L., SABLIOVSCHI, M., VIDACOV, C., J. Thermal. Anal., **24**, 1982, p.83

17. SCHNEIDER, I.A., Cinetică chimică, Editura Didactică şi Pedagogică, Bucureşti, 1974 , a) p.11, b) p.100

18. STEINFELD, J.I., FRANCISCO, S., HOSE, W.L., Chemical Kinetics and Dynamics, Second Edition Prentice Hall Upper Saddle River, New Jersey 07458, 1999, p.1

19. DÂRŢU, D., ODOCHIAN, L., Rev. Chim.(Bucuresti), **57,** no.8, 2006, p. 82

20. ODOCHIAN, L., DRAGOMIR, L., DUMITRAŞ, M., Anal. St. Univ. Iaşi, Chimie **VIII**, nr.1, 2000, p. 15

Manuscript received: 10.09.2009